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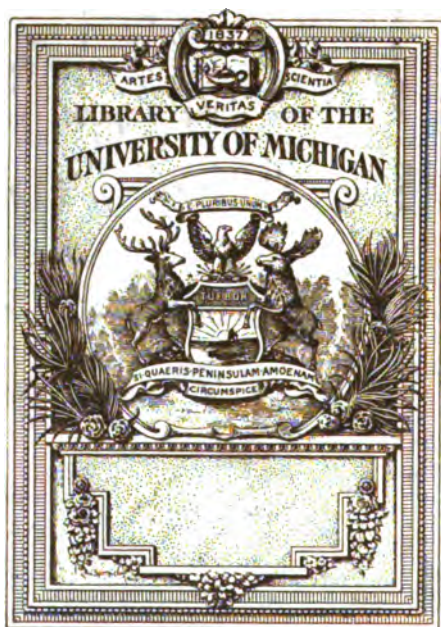
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A  
THEORETICAL AND PRACTICAL TREATISE  
ON THE 5-7116  
MANUFACTURE  
OF  
SULPHURIC ACID AND ALKALI,  
WITH THE  
COLLATERAL BRANCHES.

BY  
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*SECOND EDITION, REVISED AND ENLARGED.*

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VOLUME III.



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# P R E F A C E

TO VOLUME III.

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**THIS** volume completes the Second Edition of the Treatise on the Manufacture of Sulphuric Acid and Alkali, to which I have devoted the greater part of my available time during the past five years. To this volume the remark applies even more forcibly than to the first two volumes, that this is not merely a "new edition," but practically a new book altogether, for which the first edition has but served as groundwork. Only a few chapters resemble those of the first edition, viz. : those treating of the old chlorine process, the Weldon process, the manufacture of bleaching-powder and chlorate of potash ; and even these contain a large number of improvements and additions. The chapters on ammonia-soda, on the more recent soda-process, on the Deacon process, and the other chlorine processes, have had to be entirely re-written, and electrolysis now appears for the first time.

As before, I have been assisted by a multiplicity of observations at factories and communications from their owners and managers ; and I may claim that this work, apart from the endeavour to furnish a digest of everything which has been published on the subject, is anything but a writing-table compilation. I have certainly encountered many more difficulties than in the case of

the first two volumes. For these I was able to utilize nearly all the communications derived from actual practice, since the industries of sulphuric acid, of the other acids, and of Leblanc soda are only exceptionally hedged round with secrecy. But this secrecy is very prevalent in the majority of the industries treated of in this volume, especially the ammonia-soda, the Deacon process, and the electrolytical processes. It is true that I have had the advantage of being behind the scenes to a greater extent than very many chemists, and I believe that but little in this department has been concealed from me. But circumstances impose upon me more or less discretion in utilizing most of what I have seen or heard, and I have honestly tried not to abuse the confidence placed in me in that respect. The knowledge acquired under such circumstances has been carefully employed to avoid mistakes, and to dwell somewhat more fully than I otherwise might have done on some patent specifications and the like. In doing this, I have found that there are very few of what practical men take to be important secrets which are not accessible in print in one shape or another, or else are known just as well to other practical men. Very often I have found that the substance of communications which I had received as "strictly confidential" was to be obtained in a far more accurate and explicit form in patent specifications or other publications, open to the whole world, or else that the identical matters were treated by other professional men as well-known to everybody concerned. Taking this into account, I have found myself enabled, without any violation whatever of the discretion imposed upon me, to present a faithful picture of the actual state of the industries in question.

I must draw special attention to the fact that the copious Addenda, forming the conclusion of this volume, bring the contents of the two preceding volumes up to date, which is especially important in the case of *Sulphuric Acid*, the second edition of Vol. I. having been published as far back as 1891. Vol. III. therefore practically offers, in connection with Vol. I., a third edition of this section.

The Second Edition of this work exceeds the first in extent by one-half, and its bulk would be even considerably greater if I had not in many cases referred to the first edition for the detailed description of processes now obsolete. As it is, I could not help describing much that is no longer in practical use, together with many details which have not yet stood the test of practice, and probably never will do so. In a work like this the author cannot avoid either the former or the latter apparent diffuseness, and does not profess to do so. Those who work in this field should find here a survey of the entire ground, and are spared the trouble of trying to hunt up for themselves all the materials published in various languages. At all events, it has been my endeavour to relieve my professional brethren of this laborious work, if not entirely, at least to a very great extent. In the preface to the first edition of Vol. I. (reprinted in the second edition), I have stated the limits within which I have thought it right to confine my efforts in this direction.

I have in this edition entirely omitted the estimates for erecting alkali-works, which fill pages 323 to 332 of the first edition of Vol. III., although for these I have received many expressions of thanks. But I had to take into consideration that, during the twenty years since I have ceased to be a practical alkali

manufacturer, many changes have taken place, not merely in the prices of materials and labour, but also in the modes of building and construction. I could not therefore have undertaken on my own account to readjust those estimates so as to render them really useful at the present day, and I did not care to assume the responsibility for the work of somebody else, which at the best could be accurate only for a certain locality.

A few special remarks must be made as to the treatment adopted in the new chapter on Electrolysis. Some will here find more, others less than they require. Fault will perhaps be found with my giving a theoretical introduction, which neither does nor is intended to exhaust the subject. But I believe that this theoretical introduction, which is written in a "popular" style, will be welcome to many of my readers, without unduly swelling the bulk of the work. On the other hand, I had to quote a number of proposals which, with a few exceptions, in all probability have no future before them, without being able to criticize them properly. This task is at present still too difficult, and mistakes would arise here even far more frequently than with older branches of industry. Here, where everything is still in the rudimentary state, useful criticism, whether favourable or hostile, is best founded on positive or negative *results*, if such can be adduced. I had hoped to notice all patent specifications of any importance, but in most cases I could do so only in a condensed form. Further details will frequently be found in the Journal of the Society of Chemical Industry, and in the following German publications:—Fischer's 'Jahresberichte,' and Nernst and Borchers's 'Jahrbuch für Elektrochemie.'

The labour devoted to the First Edition of this book has been



amply rewarded by my receiving numerous proofs of its being acknowledged as a useful and faithful guide by those for whom it was intended. I trust I shall not appear too presumptuous if I express the hope that the Second Edition may meet with as friendly a reception. None of my readers can know better than myself that this work is very far indeed from perfection ; but every fair-thinking man will excuse occasional mistakes creeping in among such a mass of matter. I shall be content if only those who can say that they have learnt nothing of any importance from it will pronounce an adverse judgment on this book.

THE AUTHOR.

Zurich, March 1896.



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## FIRST BOOK.

# THE AMMONIA-SODA PROCESS.

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## CHAPTER I.

### HISTORICAL AND GENERAL.

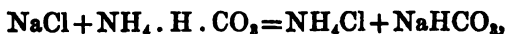
It is difficult to ascertain who was the first to produce soda by means of the reaction between ammonium bicarbonate and sodium chloride. A. Vogel (Chem. Centralbl. 1874, p. 98) says that he found a reference to that reaction in his father's notes, dating from 1822; but it evidently was quite useless there, both to himself and the world in general. Very likely somebody will bring to light a notice of that reaction written at an earlier date\*. Hundreds, nay thousands, of reactions are made, the ultimate bearing of which is not recognized by those who observed them. If the observer does not think it worth while either to publish his observation or to follow it up on a larger scale, it is lost to mankind, and no merit can be claimed for him by posterity.

We must attribute rather more value to the claims made for John Thom, chemist at Messrs. Turnbull and Ramsay's, at Camlachie (Scotland), as stated by Mond (Journ. Soc. Chem. Ind. 1885, p. 528). It has been proved that John Thom, as early as 1836, mixed ammonium bicarbonate with common salt and a little water, pressed the magma formed in bags, and made crystal soda from the solid bicarbonate remaining behind; from the mother liquor he made ammonium bicarbonate by evaporating, mixing with chalk, and heating in a retort. We are told that he

\* We cannot acknowledge this to have been done by Lucion, Chem. Zeit. 1889, p. 627, who founds a claim for Fresnel, based on some entirely indistinct allusions in a private letter written in 1811.

manufactured 2 cwt. of soda crystal per day in this manner (but, as we see from the same Journal, 1887, p. 699, only by mixing his product with Leblanc soda), but he did so only during a twelvemonth. He then left the above works, where he enjoyed a yearly salary of £30, and did not pursue the process further. Evidently he was unaware that he had found a practicable or valuable process, for he did not think it worth while to patent it, or to take care that it should become known and the inventor's merit attributed to him. His work therefore remained fruitless, and cannot in the least diminish the merit of the two inventors mentioned below, who carried on their investigations without being aware of Thom's labours.

These two are H. G. Dyar and J. Hemming, chemists, residing in London, who on June 30th, 1838, took out an English patent, distinctly setting forth the simple reaction:



and describing technical means for carrying it out on a large scale. Only then did the world obtain a knowledge of that process, which has indeed not made much chemical progress since. These investigators cannot be deprived of the honour of having been the real inventors of the ammonia-soda process as a manufacturing operation.

Dyar and Hemming mixed a saturated solution of common salt with an amount of powdered commercial ammonium carbonate equal in weight to the salt. The ammonium salt being only sesquicarbonate (mixed with ammonium carbonate), they rightly remark that bicarbonate would be preferable. The decomposition takes place according to the above equation; and the solution formed is separated from the precipitated salt. The latter is chiefly sodium bicarbonate, mixed with a little ammonium carbonate, which is driven off by heating to  $375^\circ\text{C}.$ , along with any ammonium chloride present and half the  $\text{CO}_2$  of the  $\text{NaHCO}_3$ : all this is condensed in a lead chamber; and very pure soda remains behind. On the other hand, the solution contains chiefly ammonium chloride with a little sodium carbonate, sodium chloride, and ammonium carbonate. The latter is expelled by boiling and condensed in the lead chamber; the solution is boiled down to dryness, and the residue heated with calcium carbonate, whereby the ammonium chloride is transformed into carbonate, which is

conveyed into the said lead chamber. The contents of the latter are used over again for converting common salt into soda; so that nothing but limestone is used up. (This process, as described, could not have been carried out without considerable loss of ammonia.)

A little later we find a French patent by Delaunay (March 27th, 1839), which, according to Mond, is a literal translation of the just mentioned patent of Dyar and Hemming, proving Delaunay to have been merely an agent. Hence the certificate of addition, taken out by Delaunay on May 18th, 1840, must have also proceeded from Dyar and Hemming, although they did not take out a corresponding English patent, probably on account of the expense. This additional patent, quoted by Mond *in extenso*, is extremely interesting, since it contains every important principle of the present ammonia-soda manufacture, and we will therefore quote some details from it.

*Preparation of the Carbonate of Soda.*—To a concentrated solution of sodium chloride is added an equivalent proportion of ammonium sesquicarbonate. A current of carbonic acid is passed through the mixture to saturate the ammonia and to make the decomposition as perfect as possible. The saline deposit is collected in filters, drained, and washed either with water or with a concentrated solution of sodium bicarbonate. It is then submitted to pressing, or is put at once into a furnace or retort to drive off the water, the excess of carbonic acid, and the ammoniacal salts it may contain.

*Recovery of the Ammonia.*—The liquid running from the filter is put into a distilling vessel; a sufficient quantity of lime is added to decompose all the ammoniacal salts, heat is applied, and thus ammoniacal gas is obtained, which is simply dissolved in water, or passed into a concentrated solution of sodium chloride. In the former case a sufficient quantity of sodium chloride is added, relative to the alkalimetric value of the liquor; carbonic acid is then passed through to decompose the sodium chloride. If the ammonia gas is collected in a solution of sodium chloride, carbonic acid is passed through at the same time or subsequently. In this operation the ammonia must be regarded as an intermediate agent, which takes hold of the carbonic acid to give it off again to the sodium chloride; and to make this process economical the principal object should be the preservation of the ammonia.

The carbonic acid required can be economically procured by the combustion of coals or by the calcination of limestone.

Many new proposals, even such as are ultimately crowned with success, remain a long time only on paper; but it was different with Dyar and Hemming's process. They themselves at once erected a small experimental works at Whitechapel, to which Dr. Sheridan Muspratt and Mr. James Young, of paraffin fame, paid several visits. The latter in 1840 built a somewhat large works for Mr. James Muspratt at Merton; but after two years this was abandoned, on account of excessive loss of ammonia, after expending £8000 over it. About the same time experimental works were erected by Kunheim at Berlin, Seybel near Vienna, and Bowker near Leeds; none of them existed for any length of time, but the last at least put its alkali into the market for several years. In 1840 (April 1st) Canning took out a French patent (through Delaunay) for the introduction of carbonic acid; and this was done in England by Waterton on August 27th, 1840 (No. 8608). Somewhat later came the patent of Grinus, of Marseilles (February 14th, 1852), who prescribes cooling the liquors by a refrigeration machine, and using over again the  $\text{CO}_2$  given off in calcination. Chisholm prescribes distilling muriate of ammonia, from the purification of gas, with chalk or lime, and passing the gas (in the second case together with  $\text{CO}_2$ ) into a solution of common salt (No. 443, 1852).

From that time onwards inventors in that line principally aimed at the construction of more perfect mechanical plant for mixing the gases and liquors and for more thoroughly preventing any loss of ammonia. Gossage's patent of 1854 (No. 422) will be referred to later on. He was followed by Turck (French pat., May 26th, 1854, January 29th, and December 13th, 1855): his process is stated to have been unsuccessfully tried by Nicklès, from 1865 to 1867. Then come the English patents of Schlösing (No. 1425, 1854) and H. Deacon (by the agent Johnson, No. 1504, 1854). The latter in 1854 joined with Holbrook Gaskell in erecting an ammonia-soda works at Widnes, which was carried on for about two years; after spending over it £5000 or £6000, it was reconstructed into the Leblanc alkali works, which has become so famous. The apparatus used there is said to have resembled those of Schlösing and Rolland, except that the carbonic acid was introduced under pressure. Pure carbonic acid

was to be prepared by passing fuel gases under pressure into a solution of potash or soda, and decomposing the bicarbonate formed by heating. (This part of the process has become better known by the much later patent of Ozouf, No. 1498, 1864.)

In 1855 (No. 418), Bellford patents a communication, the only "novelty" of which consists in obtaining from the impure bicarbonate pure soda by mixing it with water and submitting it to pressure, in case of need repeatedly; the solution was to be distilled, the ammonia condensed and submitted in a coke-tower to the action of carbonic acid from a lime-kilm.

Under No. 1963, 1855, Gossage patents the manufacture of ammonium bicarbonate by distilling the solution of sesqui- or monocarbonate, and the employment of the product of distillation, either in the state of vapour or after condensation, for decomposing common salt.

In 1857 (No. 2616), Bell patents the introduction of the gases from the dry distillation of leather or bones, after separating the tar, into solutions of salt for precipitating sodium bicarbonate. The novelty was to consist in the direct utilization of the distillation-gases; but this would hardly be practicable, on account of their impurities.

Schlösing's before-mentioned patent had essentially the following purpose. In horizontal cylinders, provided with an agitator, a solution of common salt is saturated with  $\text{CO}_2$  and  $\text{NH}_3$ , and the unabsorbed  $\text{NH}_3$  retained in coke-towers by a mixture of  $\text{CaCl}_2$  and  $\text{HCl}$ ; the  $\text{NaHCO}_3$  was to be dried in a centrifugal machine, washed with a solution of pure sodium bicarbonate, and heated in a horizontal iron retort, in which an Archimedean screw slowly moved it along from the entrance end to the exit end. The escaping  $\text{CO}_2$  was to be utilized for the next operation; and the  $\text{CO}_2$  further required was to be furnished by a lime-kilm which at the same time heated the retort. With 100 parts of water 30 to 33 parts of common salt,  $8\frac{1}{2}$  to 10 parts of  $\text{NH}_3$  gas, and an excess of  $\text{CO}_2$ , were to be employed.

In 1885 Schlösing, together with Rolland, erected a small works at Puteaux near Paris, where they made 86 tons soda-ash in the first year and 230 tons in the second year; that factory, which of course could only be looked upon as an experimental works, was stopped in 1857. Soon after Schlösing and Rolland took out another English patent (No. 644, 1858), chiefly in order

to make the process perfectly continuous. In the same apparatus, whilst a certain quantity of salt was converted into bicarbonate and removed from the vessel, a corresponding quantity of fresh NaCl was to be introduced, and the corresponding quantity of  $\text{NH}_3$  recovered from the filtering liquor and admitted into the brine; lastly, by calcining the bicarbonate and burning limestone the requisite quantity of  $\text{CO}_2$  was to be obtained. They described their process at length in the *Ann. Chim. Phys.* [4] xiv. p. 5 (1868). Their apparatus consists of four or more horizontal cylinders, communicating with each other. Into one of these a solution of 30 parts NaCl in 100 water enters, circulates through all four cylinders, and runs out of the last one. To this solution 22 parts of ammonia, either in the gaseous state or dissolved in water, are admitted in the second cylinder. On travelling further the liquor is brought into contact first with lime-kiln gases, and at last with the  $\text{CO}_2$  obtained by heating the bicarbonate and the liquid filtered from it. Within the cylinder are placed a kind of paddle-wheels for distributing the liquid and facilitating the absorption; the cylinders are cooled on the outside by water. The gases are aspirated in the direction opposite to the flow of the liquid by a fan-blast, which at the same time causes a partial vacuum and prevents the escape of ammonia out of the joints. In order to retain the ammonia gas which escapes absorption (of which a portion remains already in the first cylinder, filled with pure NaCl solution), the exit gases are passed through a coke-tower fed with water; and this is afterwards employed for dissolving salt. From the last cylinder the solution of  $\text{NH}_4\text{Cl}$  runs away along with the precipitated  $\text{NaHCO}_3$ ; these are separated by a centrifugal machine and washed with a little water (in which  $1\frac{1}{4}$  per cent. is lost by redissolving). The bicarbonate is dried and ignited in the above-mentioned cylindrical retort with Archimedeal screw, and the  $\text{CO}_2$  gas drawn off by an aspirator. The liquid separated from the bicarbonate is heated by steam to  $60^\circ$  or  $70^\circ$  C., to expel the  $\text{CO}_2$ , and then to  $100^\circ$  C. to expel the ammonia. It is next heated with milk of lime in a horizontal cylinder provided with an agitator; thus  $\text{NH}_3$  is liberated, which is deprived of water by cooling and re-introduced into the converting-apparatus. From 167 parts NaCl 100 only  $\text{Na}_2\text{CO}_3$  are obtained, instead of 151 indicated by theory. For making 100 kilog. of anhydrous soda the following quantities are stated to have been required:—

kilog.

167·0 NaCl = 180 kilog. crude salt or 5·57 hectolitres of saturated brine;

68·5 CaO = 122 kilog. limestone, = 135 kilog, with 10 per cent. moisture.

32·0 NH<sub>3</sub>, of which at most 1 kilog. was lost.

128·3 coals for distilling and steam;

72·0 coke for the lime-kiln and for heating bicarbonate.

To this must be added frs. 1·40 for labour, and frs. 8·7 to 9·67 for general expenses, inclusive of 6 per cent. interest, according to the size of the works. This cost price, according to an estimate made by Scheurer-Kestner (Bull. Soc. Chim. xlv. p. 307), would have amounted to 21 frs. per 100 kilog. when employing common salt, or 20 frs. when employing brine. Since at that period, according to Mond (in the paper quoted on p. 1), the selling-price of soda-ash in France was 65 or 70 frs., and the salt-tax only amounted to 10 frs. for 100 kilog. salt or 18 frs. for 100 kilog. soda-ash, there must have been an enormous margin for profit; and there is absolutely nothing to justify the statement made by the inventors in their above quoted paper in 1868, that they had been compelled to give up the manufacture on account of "fiscal difficulties," considering that they had to pay the salt-tax on 180 kilog., for each 150 kilog. used by the Leblanc alkali-makers. This would only amount to 3 frs. per 100 kilog. alkali, which was not worth speaking of in the face of that alleged low cost-price. This has been pointed out by Solvay in 1878, and by Mond in 1885 (*loc. cit.*); nor has Scheurer-Kestner, in his above-quoted paper, explained this contradiction. It is therefore incredible that Schlösing and Rolland worked as cheaply as they alleged in 1868; for in that case they must have found ample capital for a manufacture realizing such an enormous profit. Undoubtedly they wasted much more ammonia than they confess to; and probably their mechanical arrangements did not turn out to be practicable either.

The latter point is made evident by the fact that the same inventors took out the above-mentioned new patent, which embodies most incisive alterations of plant, and that in 1858, a year after closing their works. They claim to have been the first to have introduced a continuous system of working; but supposing this to be correct, it was only done on paper. If they had as much as tried to carry it out in practice, it would undoubtedly

have been mentioned by Scheurer-Kestner, the avowed object of whose paper is to point out the merit of his compatriots as compared with those of the English inventors. Evidently the patent of 1858 has never emerged into practice; nor can any particular merit be claimed for publishing it later on in 1868, when it had lapsed for a long time—certainly none which justifies the special honours which have been claimed for these two men in comparison with many others who have achieved quite as much in the same line. Only the pre-eminent respect justly paid to Schlösing as a *savant*, and the energetic claims made for his process by his pupils and friends, have caused his process to be represented as a very important stage in the history of that industry, a representation not borne out by the facts. Mond justly points out that Schlösing and Rolland's experiments were no more successful than those of their predecessors—that they were not carried out on any larger scale, nor persevered with for a longer period.

In 1858 Heeren (Dingl. Journ. cxlix. p. 47) made an experimental research on the ammoniacal soda process. At the outset he makes the curious proposal to obtain pure  $\text{CO}_2$  from limestone and muriatic acid; but where is the latter to come from, if the soda is to be made by the ammonia process? He further proposes purifying the brine from magnesia and lime by soda, filtering and saturating the clear liquor with  $\text{NH}_3$  gas, viz. 44 parts  $\text{NH}_3$  to 100  $\text{NaCl}$ , by which only  $\frac{2}{3}$  of the latter is decomposed; so that from 100  $\text{NaCl}$  only 105, instead of 158,  $\text{NaHCO}_3$  is formed. If only one equivalent of  $\text{NH}_3$  to two  $\text{NaCl}$  is employed, the decomposition proceeds up to  $\frac{4}{5}$  of the ammonia salt, the excess of salt being lost; but this is better than the opposite way, in which much  $\text{NH}_3$  would be lost. Now  $\text{CO}_2$  is passed into the liquid, which is very slowly absorbed unless assisted by pressure. The separation of the solution of  $\text{NH}_4\text{Cl}$  from the precipitate of  $\text{NaHCO}_3$  takes place as usual. The solution is distilled with lime, and the  $\text{NH}_3$  condensed in brine, if fresh salt can be dissolved at the same time; if only brine is at disposal, the  $\text{NH}_3$  gas must be deprived of water by cooling. If the ammonia is to be obtained as carbonate, the solution of  $\text{NH}_4\text{Cl}$  is boiled down to dryness, mixed with twice its weight of chalk and damp clay (the latter in order to remove the fused  $\text{CaCl}_2$  more easily from the vessel), and heated to a low red heat in iron retorts. According to Heeren's



calculation, 1 cwt. of this soda-ash would cost 12s. 3d., without counting general expenses and muriatic acid; with these it would cost 16s. 6d. The bicarbonate would cost 14s. 6d. without, or 13s. per cwt. with HCl; this price is higher, because the manufacture must be conducted on a smaller scale.

To Heeren is due the merit of having for the first time made a scientific investigation of the reactions of the ammonia-soda process. We cannot blame him, looking at the time he wrote, for the insufficiency of his practical proposals.

The further history of the ammonia-soda manufacture is undoubtedly connected from the very first with the name of Solvay. Ernest Solvay (whose brother Alfred also deserves great credit for developing the process, but chiefly in the business line) seems to have conceived the first idea of his process as early as 1861. According to his statement (as quoted, *e. g.*, by Scheurer-Kestner, *loc. cit.*), he took out a patent on April 15th, 1861, but probably only in his own country, Belgium. The first English patent dates December 11th, 1863 (No. 3131); his first French patent November 19th, 1863 (No. 60920); nor is any earlier patent referred to in these or later patents of his. The first factory working according to his process was erected in 1863, at Saint-Josse-ten-Node, near Brussels, a larger one at Couillet, near Charleroi, in 1865. I have it from Solvay himself that he was originally under the impression that he had been the first to discover the reaction of the ammonia-soda process, and that *à fortiori* he was ignorant of the number of experiments made with it in various countries, all of them unsuccessful and connected with heavy losses. Had he known this, he would certainly not have had the courage to devote himself to the task, and that with all energy, at the risk of losing all his fortune and drawing upon that of his relatives. It required not merely ordinary energy and pre-eminent mechanical skill, such as Solvay certainly possessed, but an almost fanatical belief in the enormous value of his inventions, to battle with many years' failures and heavy losses, till his conception had ripened to its splendid realization. Already in 1867 he exhibited his soda in Paris, but he received only a bronze medal, and that rightly, for his process was then still far from having proved its permanent vitality, and the Jury could certainly not appraise him any higher than many of his predecessors, whose factories had been in operation for several years.

During the next few years Ernest Solvay, with the co-operation of his brother Alfred and of M. Hanrèz, greatly improved the apparatus, and in 1872 he was in a position to lay out a factory, on a scale which may be looked upon as colossal for that period, at Varangéville, near Nancy. This factory started working in 1873, and convinced the world that there was no more doubt of a perfect success. The new forms of his apparatus are described in the English patent, No. 1525, 1872; many improvements are found in Nos. 999, 1904, 2143, all of 1876, and in many subsequent patents, to be mentioned in the following chapters.

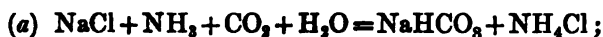
We must point out here that most apparatus patented by Solvay are very ingeniously planned, but too complicated; some have never been in actual use, and others have been replaced by much simpler arrangements, employed by other manufacturers before him or at the same time with him, as we shall see later on. Among Solvay's original ideas, that of the carbonating-tower seems to be the only one which is still employed, and that in an essentially modified shape. This invention, the one which is most intimately connected with his name, and which is applied at all the numerous works belonging to the Syndicate bearing Solvay's name, may have been conceived somewhat earlier; but only those improvements which had been patented in 1872 made the process successful, to such an extent that Solvay received in 1873 the diploma of honour at the Vienna Exhibition, and only then the conviction became general that the Leblanc process had met with a powerful or even a victorious rival. I will therefore conclude my historical sketch at this point, and leave all later inventions (together with some previous ones) to be noticed when describing the single operations.

It follows from the above remarks that Solvay's inventions, ingenious as they are, do not represent the *only* solution of the problem in question; on the contrary, there exist a number of ammonia-soda works, carried on successfully and profitably, with apparatus differing totally from Solvay's, and preferred by their owners to his, although the patents are now lapsed. How far this preference is justified we cannot decide, more particularly as very few manufactures are surrounded with greater secrecy than the ammonia-soda; but the contrary cannot be concluded from the enormous financial success of the Solvay Companies, for which other than merely technical factors must have co-operated.

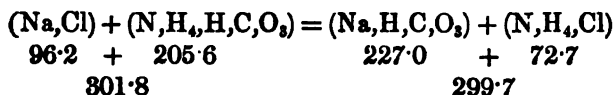
It may be of interest to mention that in 1872 Solvay's daily make was 10 tons of soda with two "units." The English works of Messrs. Brunner, Mond, & Co. was at once laid out with 20 ton units, and later on they got up to 60 ton units (Mond, Journ. Soc. Chem. Ind. 1885, p. 527).

*Theory of the Ammonia-Soda Process.*

Comparing this theory with the many divergent opinions relating to the true theory of the Leblanc process, that of the ammonia-soda process appears to be very simple indeed. It can be expressed in one of the two following formulæ, which have practically the same meaning :



The form (a) corresponds best with the method followed by Solvay and most other inventors; form (b) with Schlösing's new process. In reality, however, the matter is not so simple as it looks. Even a thermochemical consideration of the reaction shows that the tendency for carrying it out cannot be a strong one. If in equation (b) we introduce the heat of formation of all the four salts concerned from their elements, we find :—



That is to say :—The heats of formation are almost identical for both sides, and, as they stand here, that of the newly formed bodies is even slightly below that of the original substances. We must, however, consider that generally the accuracy of thermochemical data is not sufficient to justify any conclusions to be drawn from such a slight difference, and that, moreover, those data may vary with the temperature to such an extent that a small deficiency may be converted into a small surplus.

All things considered, the thermochemical data, as well as all known facts, prove that we have to deal with a *reversible reaction*, to be formulated thus :—



This reaction depends upon two conditions, connected with each

other, whether it will run in the direction of one or the other of the two arrows. The first is the *action of mass*, that is the excess of one or the other of the reagents: the other is the question, which of the four possible salts will be *removed from the sphere of action*, either in the solid or in the gaseous state, under the circumstances of the case. Whatever is thus removed from solution is therefore withdrawn from further reaction in the inverse sense, which tends to direct the remaining substances to a further formation of the same body, by the action of mass.

In the present case, that condition which in the first instance directs the reaction in one or the opposite way is the *temperature*. At a low temperature the tendency is greatest for the reaction to run with the arrow  $\longrightarrow$ , since it is favoured by the precipitation of difficultly soluble sodium bicarbonate. But at a higher temperature, or else under circumstances favouring the action of *evaporation* even at lower temperatures, the reaction must run in the opposite direction  $\longleftarrow$ , since the only volatile salt among the four in question is ammonium bicarbonate: it does not concern us here that this substance does not evaporate as such, but at once dissociates into  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ .

We must, however, abstain from the conclusion that the temperature for directing the reaction in the sense  $\longrightarrow$  should be as low as possible. At too low a temperature not merely sodium bicarbonate, but all the other three salts would partly separate out in the solid state, and this soon puts a limit to the practically possible lowering of the temperature. In fact, it is not possible under any circumstances to cause the whole of the sodium bicarbonate to crystallize free from the other bodies; and the reaction  $\longrightarrow$  would be much too incomplete from the outset if the two reagents  $\text{NaCl}$  and  $\text{NH}_4 \cdot \text{H} \cdot \text{CO}_3$  were to be employed exactly in molecular proportions. Nothing remains but to promote reaction  $\longrightarrow$  by the action of mass, which in practice is simply effected by leaving a considerable portion of  $\text{NaCl}$  undecomposed.

We have already seen that Heeren and Schlösing found that the conversion of  $\text{NaCl}$  into  $\text{NaHCO}_3$  stops at  $\frac{2}{3}$  or  $\frac{1}{2}$  of the whole. In one of his earlier patents Solvay maintained that he decomposed the salt almost completely, but he must have recognized this very soon to be erroneous. Al. Bauer (Deutsche chem. Ges. Ber. vii. p. 272) shows that this incompleteness of the decomposition is not merely due to the solubility of sodium bicarbonate, as was

previously supposed, but to the fact that the carbonates of sodium may mutually decompose with ammonium chloride into ammonium carbonate and sodium chloride, and that under very varying circumstances:—*e. g.* on the spontaneous evaporation of a solution of  $\text{NaHCO}_3$  and  $\text{NH}_4\text{Cl}$  at from  $8^\circ$  to  $15^\circ$  C.; also on their spontaneous evaporation in a current of  $\text{CO}_2$ ; and also with not fully concentrated solutions, saturated with  $\text{CO}_2$ , when exposed to a temperature of  $-15^\circ$  C. The reaction then takes place in the sense  $\leftarrow$  (p. 11), and this is completed at a higher temperature.

Günsberg (*ib.* vii. p. 644) noticed the same inversion of the reactions of the ammoniacal soda-process in all his experiments; he takes it as a matter of course, considering the volatility of ammonium carbonate and the solubility at different temperatures of the salts in question. That portion of  $\text{NaHCO}_3$  which remains dissolved in the  $\text{NH}_4\text{Cl}$  solution will be always lost; and care will have to be taken that from the very first a saturated solution of  $\text{NH}_4\text{Cl}$  is obtained which at a certain pressure contains the minimum quantity of sodium compounds. He found that at ordinary temperature and pressure 100 parts of a  $\text{NH}_4\text{Cl}$  solution, saturated at  $17^\circ$  C., contain dissolved 25.89 parts  $\text{NH}_4\text{Cl}$  and 5.742 parts  $\text{NaHCO}_3$ . This will be the case when at the ordinary temperature 58.5 parts of  $\text{NaCl}$  are treated with 180 parts of a liquor containing 10.396 per cent.  $\text{NH}_3$ .

According to Honigsmann's experiments (quoted by Landolt in Hofmann's Vienna Exhibition Report, 1875, i. p. 452):—

I. A solution containing per litre

265 grams  $\text{NaCl}$  (= 104 grams  $\text{Na}$ ) and

77 „  $\text{NH}_3$  (= 1 eq.  $\text{NaCl}$  : 1 eq.  $\text{NH}_3$ ),

after being saturated with  $\text{CO}_2$  at  $15^\circ$  C. under ordinary pressure, yielded:—

(a) a precipitate consisting of

251 grams  $\text{NaHCO}_3$  (= 69 grams  $\text{Na}$ ) and

33 „  $(\text{NH}_4)\text{HCO}_3$  (= 7 „  $\text{NH}_3$ );

(b) a solution containing

35 grams  $\text{Na}$  as  $\text{NaCl}$  or  $\text{NaHCO}_3$ , and

70 „  $\text{NH}_3$  „  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)\text{HCO}_3$ .

II. On passing  $\text{CO}_2$  into a solution containing per litre 331 grams  $\text{NaCl}$  ( $=130 \text{ Na}$ ) and  $70.8 \text{ NH}_3$  ( $=4 \text{ NaCl} : 8 \text{ NH}_3$ ) there were obtained :—

(a) a precipitate of

286.2 grams  $\text{NaHCO}_3$  ( $=78 \text{ Na}$ ) and

15 „  $(\text{NH}_4)\text{HCO}_3$  ( $=3.2 \text{ NH}_3$ ) ;

(b) a solution of

52 grams  $\text{Na}$  as  $\text{NaCl}$  or  $\text{NaHCO}_3$  and

67.5 „  $\text{NH}_3$  „  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)\text{HCO}_3$ .

Accordingly, there have been converted into bicarbonate, of each 100 parts  $\text{Na}$  employed as  $\text{NaCl}$ ,

in exp. I. ( $\text{NaCl} + \text{NH}_3$ ) 66 parts,

„ II. ( $4 \text{ NaCl} + 3 \text{ NH}_3$ ) 60 „

Calculated for ammonia, there were precipitated as bicarbonate, upon 100 parts of  $\text{NH}_3$ ,

in exp. I. ( $\text{NaCl} + \text{NH}_3$ ) 90 parts  $\text{Na}$ ,

„ II. ( $4 \text{ NaCl} + 3 \text{ NH}_3$ ) 110 „ „

In experiment II. much less ammonium bicarbonate was precipitated along with the sodium bicarbonate than in I. [These experiments would seem to prove that the best proportion is 4 molecules  $\text{NaCl}$  to 3 molecules  $\text{NH}_3$ ; but this is at variance with Günsberg, who requires  $18.72 \text{ NH}_3$  for  $58.5 \text{ NaCl}$ , i. e. much more than an equivalent. We shall see that under no circumstances is it possible to work at  $15^\circ$  in real practice.]

For the theory of the ammonia-soda process we must also take notice of the experiments made by Reich on the solubility of sodium bicarbonate in solutions of sodium chlorides, quoted Vol. II. p. 54.

Further investigations on the theory of that process have been made by Schreïb (Zsch. f. angew. Ch. 1888, p. 223 ; 1889, pp. 445 & 486). He could never precipitate more than four-fifths of the sodium present. The proportion in which this can be done depends on the proportion between  $\text{NH}_3$  and  $\text{NaCl}$ , further upon the temperature, but scarcely at all upon the pressure. He investigated in the first respect the *influence of ammonia on the solubility of sodium chloride*. 1 litre of saturated solution of  $\text{NaCl}$  at  $15^\circ \text{C}$ .

contains 317·8 grams NaCl=81·78 per cent. by volume, but in the presence of  $\text{NH}_3$  only the following percent. NaCl by volume :—

$\text{NH}_3$ p. c. by vol.	NaCl p. c. by vol.	$\text{NH}_3$ p. c. by vol.	NaCl p. c. by vol.	$\text{NH}_3$ p. c. by vol.	NaCl p. c. by vol.
3·5	29·5	6·5	27·7	9·5	25·7
4·0	29·2	7·0	27·4	10·0	25·4
4·5	28·9	7·5	27·1	10·5	25·1
5·0	28·6	8·0	26·8	11·0	24·8
5·5	28·3	8·5	26·4	11·5	24·4
6·0	28·0	9·0	26·1	12·0	24·1

Only one solution is possible, *saturated* with NaCl, and at the same time containing exactly 1 mol. NaCl to 1 mol.  $\text{NH}_3$ , viz., that containing 7·8 volume per cent.  $\text{NH}_3$  to 26·8 vols. per cent. NaCl. In manufacturing practice, of course, solutions occur which contain less NaCl than they could dissolve according to the  $\text{NH}_3$  present. Schreib made some laboratory experiments with solutions of various concentrations, at the temperature  $18^\circ \text{C}$ ., all of which he carbonated thoroughly. With *concentrated* solutions his results were as follows :—

Original Solution.				Carbonated Solution.					
No.	Degree Baumé.	$\text{NH}_3$ p. c.	NaCl p. c.	Degree Baumé.	$\text{NH}_3$ p. c.	NaCl p. c.	$\text{NH}_4\text{Cl}$ p. c.	Percent. Decom- position.	$\text{Na}_2\text{CO}_3$ grams per litre.
1	22·4	3·4	29·6	21·4	0·6	20·1	9·1	33·1	90·0
2	21·0	4·5	29·1	20·2	1·0	17·9	10·8	40·0	...
3	20·8	4·9	28·6	...	...	14·8	14·9	52·3	...
4	19·1	5·9	27·9	...	...	11·0	16·8	62·5	...
5	19·0	6·1	27·6	17·2	0·7	11·0	16·4	62·0	...
6	19·0	6·3	27·4	17·1	1·2	10·9	16·4	62·5	138
7	18·9	6·6	27·3	...	1·3	10·2	16·1	63·1	146
8	18·7	6·8	27·4	...	...	9·9	19·0	67·6	156
9	18·4	7·2	27·2	...	1·3	9·3	17·9	67·8	154
10	17·4	8·9	25·8	...	1·3	7·4	18·8	73·6	168
11	14·4	11·5	24·3	...	1·3	7·3	18·5	73·6	145
12	13·4	13·2	23·5	...	2·9	9·5	14·2	62·0	132

The results obtained on the manufacturing scale will not be identical with those shown above, but we can clearly discern the right way. With a low percentage of  $\text{NH}_3$  the carbonation goes on rapidly, but the yield is small, much salt is lost, and a large bulk

of liquid must be distilled. With a very high percentage the yield is greater and the loss of salt smaller, but more  $\text{NH}_3$  is needed, the carbonation goes on more slowly, and the work is improved by ammonium carbonate being carried away and causing obstructions. The limits of the solutions employed in practice are between No. 3 and Nos. 9; No. 6 and 7 are probably best. In practice the carbonation cannot be as thorough as in these experiments, and the maximum percentage decomposition of 73.6 will hardly ever be obtained. There is also a loss of soda in washing the precipitated bicarbonate, which in the laboratory amounts to 5 per cent., in practice to 10 per cent. and upwards.

The following experiments were made with *dilute* solutions, corresponding in respect of their  $\text{NH}_3$  to the same numbers of the first series :—

Original Solution.				Carbonated Solution.					
No.	Degree Baumé.	$\text{NH}_3$ p. c.	$\text{NaCl}$ p. c.	Degree Baumé.	$\text{NH}_3$ .	$\text{NaCl}$ .	$\text{NH}_4\text{Cl}$ .	Percent. Decom- position.	$\text{Na}_2\text{CO}_3$ grams per litre.
4	15.8	5.9	22.9	...	...	7.4	15.2	69.1	...
8	13.6	6.8	20.5	...	...	5.9	14.7	70.3	...
9	14.8	7.2	22.6	...	...	6.9	15.3	70.5	...

Here the decomposition is rather more complete for the same percentage of  $\text{NaCl}$ ; but this advantage is more than compensated by more difficult carbonation, smaller yield, and higher cost. Such dilute solutions are hardly ever used in practice.

Whilst in theory 100 parts soda-ash of 97 to 99 per cent. correspond to 110 parts of pure  $\text{NaCl}$ , or 115 of common salt (in England, say, 120 of damp salt), in practice at least 200, usually 220 or sometimes more, parts of salt are used, but the figure 220, involving a loss of 100 parts of salt, ought never to be exceeded.

Solutions of ammonia, saturated with  $\text{NaCl}$ , when carbonated are able to dissolve a further quantity of  $\text{NaCl}$ , as the conditions are now changed, and  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{H.CO}_3$  have taken the place of  $\text{NaCl}$  and  $\text{NH}_3$  and a large proportion of  $\text{Na}$  has been precipitated as bicarbonate (together with some ammonium bicarbonate). A carbonated solution, containing much ammonium



bicarbonate, on addition of NaCl yields a precipitate of sodium bicarbonate. Hence it is best to give from the first an excess of  $\text{NH}_3$  and to add during carbonation a quantity of solid NaCl corresponding to that excess. This solid NaCl dissolves in the same proportion as  $\text{NaHCO}_3$  is precipitated, and thus keeps the liquid in that state in which the  $\text{NaHCO}_3$  is least soluble. Thus on the small scale a decomposition of 80 per cent. can be attained. The concentrated solution is more easily carbonated and the  $\text{CO}_2$  is better utilized. [Precisely the same proposal was made by Solvay many years ago.]

Schreib also describes the following improvement:—Instead of at once distilling the liquor filtered from the bicarbonate, in which case the undecomposed sodium chloride is lost, he treats it with solid sodium chloride and gaseous ammonium carbonate (or  $\text{NH}_3$  and  $\text{CO}_2$ ), whilst strongly cooling. This causes sodium chloride and ammonium carbonate to enter into solution, and ammonium chloride to be precipitated in the solid state. In the end 100 c. c. of a saturated solution at  $5^\circ \text{C}$ . contain 25.5 grams NaCl and 4.1 grams  $\text{NH}_4\text{Cl}$ . We shall refer to this process later on.

The excess of NaCl employed for promoting the decomposition remains in the solution filtered from the solid sodium bicarbonate; this solution principally contains ammonium chloride, with some sodium and ammonium bicarbonate. During the recovery of ammonia from this mother liquor, more NaCl is formed by the decomposition going on at a higher temperature :



All this sodium chloride remains in the calcium-chloride liquor run off from the ammonia-stills, and is usually lost in this way. Only where common salt has a more than ordinary value will it pay to recover it by evaporation and fishing; but this will rarely be the case, since ammonia-soda works are usually established precisely in those localities where common salt has a very low value.

As under the most favourable circumstances the manufacture of alkali by the ammonia process always requires the expenditure of more sodium chloride than that by the Leblanc process, viz., from 20 to 50 per cent., it is evident that the former must be based on obtaining the salt at a very low price. This is all the more easily

attained, as it is unnecessary to separate the salt in the solid state, and it is quite possible to use the brine as it is pumped up.

The *lime* required for recovering the ammonia may be compared with the limestone required in the Leblanc process, all the more as that lime must be always made on the spot by burning limestone, in order to obtain the *carbonic acid* required for the process. The sulphur and nitre consumed in the Leblanc process is represented in the ammonia process merely by the loss of ammonia; all these substances serve merely as intermediary agents for decomposing the common salts, and they should be recovered to the greatest possible extent, in order to make the process economical.

The fact that this recovery cannot be carried out in the Leblanc process to anything like the same extent as in the ammonia process, and involves much greater expense, constitutes one of the disadvantages of the former compared with the latter.

A great advantage of the ammonia process is the comparatively small consumption of *fuel*. The thermochemical data (p. 11) have shown us that the principal reaction of the process is not connected with any theoretical consumption of energy; nor is this of much importance in the recovery of ammonia from the ammonium chloride, as we shall presently see. The roundabout course of the reactions, which in the Leblanc process causes so much waste of heat (Vol. II. p. 478) does not exist here. In fact, the greatest consumption of fuel in the ammonia-soda process is caused by the generation and mechanical propulsion of the carbonic acid, viz., by the coke employed in the lime-kilns and the coal burnt under the steam-boilers for driving the blowing-engine.

The recovery of ammonia is frequently effected by means of the exhaust steam from the blowing-engines, but, of course, not without some expense, since otherwise this engine can be driven much more cheaply by a condensing steam-engine (comp. Chapter VI.)

The decomposition of ammonium chloride by lime is an exothermic process, that is, one accompanied by evolution of heat; for the heat of neutralization (in aqueous solutions) is 12.27 calories for  $\text{NH}_3 + \text{HCl}$  and 13.95 for  $\frac{1}{2}(\text{CaO} + 2 \text{HCl})$ , so that an excess of 1.68 calories is to be disposed of. But much more than this, viz. 8.8 cal., is required for expelling the  $\text{NH}_3$  from its aqueous solution, and much more again in the case of a dilute solution, so that some fuel must be actually consumed here.

The *chlorine* is removed in the ammonia-soda process in a shape

representing even slightly more energy than before, since  $(\text{NaOH aq.}, \text{HCl aq.}) = 13.74 \text{ cal.}$ , and  $\frac{1}{2}(\text{CaO}, \text{H}_2 \text{ aq.}, 2 \text{ HCl aq.}) = 13.95 \text{ cal.}$  This explains the difficulty of liberating HCl or free chlorine from the calcium chloride running to waste in this process, which theoretically requires quite as much energy as the liberation from sodium chloride, whereas in the Leblanc process the chlorine is set free at once in the shape of HCl.

The importance of *recovering the ammonia* as completely as possible is illustrated by the following:—100 parts of pure  $\text{Na}_2\text{CO}_3$  is equivalent to 32.8  $\text{NH}_3$  or 162.25  $(\text{NH}_4)_2\text{SO}_4$ . But as only two-thirds of the sodium is converted into carbonate, we must assume 50  $\text{NH}_3$  or 250 ammonium sulphate for each 100 parts of sodium carbonate, or  $2\frac{1}{2}$  tons of ammonium sulphate for each ton of soda-ash. The value of the former is at present about £30 per ton, that of the latter about £4. If 99 per cent. of the ammonia entering into reaction is recovered, the 1 per cent. lost still represents a value of 6s. per ton of soda-ash. Formerly that loss was much greater; and a few years ago very few works seem to have suffered so little loss as 1 per cent. of  $\text{NH}_3$ , but nowadays the best-conducted works do a great deal better than this.

### *Synopsis of the Operations.*

In every ammonia-soda works ammonium bicarbonate must react with sodium chloride. This can be done by an infinite variety of apparatus, and the preparatory reactions, necessary in every case, can also be grouped in very different ways. The beginning is always made with sodium chloride; but quite a different course must be followed according to whether solid salt or brine is the raw material at disposal. The ammonium bicarbonate is in all cases formed during the process itself, and this also can be effected in various ways. Some, like Schloesing in his process of 1878, prepare first ammonium bicarbonate as a solid substance, and then only cause it to react with sodium chloride; most other inventors prepare an aqueous solution, containing as much sodium chloride and ammonia as possible, and treat this with an excess of carbonic acid, so that the ammonium bicarbonate, as soon as it is formed, enters into reaction with the sodium chloride, and is only recognized by the unavoidable

imperfection of the reaction (p. 11 *et seq.*). This second form of the process can be carried out in two different ways, viz., either by saturating brine with gaseous ammonia, or by dissolving solid salt in concentrated aqua ammoniæ. In all cases the free ammonia is mixed with a little carbonate; but this does not signify, as this is only normal carbonate, which does not react with a solution of NaCl.

This enumeration by no means comprises all the forms which the ammonia-soda process may take. We mention at present only the following:—The sodium salt to be decomposed need not be the chloride; it may also be the sulphate, nitrate, or other salts. The ammonia may be employed as ammonium sulphide. These less important forms of the process will be separately treated in Chapter VIII.

It is hardly necessary to say that the recovery of ammonia from the ammonium chloride is an indispensable operation, and is intimately connected with those previously mentioned.

Lastly, we shall later on notice the attempts to utilize the chlorine passing into calcium chloride. Although these attempts have not borne much fruit, they cannot be left unnoticed, and there is now a better prospect of their success than formerly.

In the following chapters the various operations will be described, without limiting ourselves to the special combination made by one or the other inventor, seeing that the various forms of each operation can mostly be combined at will with one another. In most cases we shall give Solvay's processes precedence, since perhaps nine-tenths of all ammonia-soda is made by them; but I have already remarked (p. 10) that only very few of the apparatus described in the numerous patents taken out by Solvay are still employed, at least without essential modifications and simplifications.

## CHAPTER II.

## THE AMMONIACAL SOLUTION OF SALT.

I. *Preparation of the Salt Solution.*

In exceptional cases the process is commenced with solid sodium chloride of sufficient purity. This can only be done in places where the salt has an extremely small value, *e. g.* close by rock-salt mines or by sea-salt works. At Neu-Stassfurt, rock-salt testing 98 or 99 per cent. can be had in any quantity; but it seems to be too dear for this purpose, and, at all events, it is not yet employed to any considerable extent.

At some salt-works on the south coast of France the salt extracted from sea-water by spontaneous evaporation costs very little indeed, viz., from 1*s.* to 2*s.* per ton, irrespective of duty, and this has been utilized for ammonia-soda on a moderate scale. The processes invented by Boulouvard, to be subsequently described, were intended for this special case.

In the large majority of cases ammonia-soda can only be economically produced if at least the greatest portion of the sodium chloride is present in the shape of *concentrated brine*, thus saving the expense of evaporation and re-solution. In this form salt is certainly very cheap. At Varangéville a ton of salt in the shape of saturated brine costs 2 francs, in Cheshire 6*d.*, in both cases inclusive of mining royalty and pumping. The salt thus costs next to nothing; but in France a heavy duty must be added, viz. 10 francs per 100 kilog. sodium chloride, which is levied on brine as well. In Germany salt pays no duty, if "denatured" for industrial purposes, and this rather troublesome process need not be applied to brine. Apart from brine, a little solid salt must be always employed. At Varangéville this formerly amounted to 20 per cent., but recently less solid salt seems to have been employed.

The brine must, of course, be sufficiently strong or, preferably, saturated. A saturated solution of pure sodium chloride contains

at 15° C. about 26·4 per cent. NaCl by weight, and has the specific gravity 1·2043. Exact data on the solubility, specific gravity, and all other properties of sodium chloride are given in Vol. II. p. 3; occurrence in nature and composition of salt, &c., p. 8; statistics, p. 14.

Natural brine is hardly ever *pure* enough for the present purpose. Its percentage of calcium, magnesium, and iron salts (comp. on the estimation of these, Vol. II. p. 88) is very injurious, as all these bases are precipitated by ammonium carbonate; they contaminate the sodium bicarbonate, and cannot be removed from this. The magnesia also causes trouble by forming double salts with sodium carbonate and chloride, which give rise to the formation of incrustations in the apparatus. It is hence indispensable to remove these bodies as much as possible, before the sodium bicarbonate is precipitated. This purifying process has been sometimes effected between the preparation of the ammoniacal salt solution and the carbonating, but it is best to purify the brine itself before it is treated with ammonia.

For this purpose the brine is put into large tanks, where it is mixed with a sufficient quantity of the purifying reagents. The analysis of the brine being known, at first sufficient milk of lime may be added to decompose the magnesium salts, and then sufficient ammonium carbonate to convert the calcium salts, still present in solution, into calcium carbonate and the corresponding ammonium salts. It is simpler to employ from the first a sufficient quantity of ammonium carbonate, in the shape of brine containing this salt, as it is obtained in the subsequent operations by washing the exit gases, and thus to precipitate lime and magnesia at the same time; but this requires a considerable excess of ammonium carbonate, about 22 lb.  $\text{NH}_3$  per ton of brine. This operation may be performed in iron or wooden vessels, by means of a mechanical stirrer or agitating the liquor by compressed air. After proper settling, the clear portion of the liquor is removed to the saturating apparatus. There should be at least two such vessels provided, preferably three, to allow sufficient time for settling. Of course any continuously acting system of decantation, or filter presses &c., may also be employed.

The mud collecting in the vessels is from time to time removed; as it contains a little ammonium salt, it should be passed through the ammonia-stills before being thrown away.

Mond (Engl. pat. 4175, 1874) adds to each 4300 litres of brine 36 kilog. soda-ash and 9 kilog. lime, and removes the iron by means of the ammonium sulphide formed in the distillation of crude gas-liquor.

Solvay (French pat. 130527, of 1879) purifies brine simply by adding soda-ash and heating in large bulk. If iron is present, a little bleaching-powder is added.

Wigg (Engl. pat. 3125, 1882) removes magnesia from brine by adding sodium arseniate.

Collins (Amer. pat. 459236) treats brine with an electric current not exceeding  $2\frac{1}{2}$  volts, which he believes will decompose the impurities and make them insoluble, without affecting the NaCl.

If *solid salt* (analysis, Vol. II. p. 87) is employed for bringing an insufficiently saturated brine up to strength, it may be put in together with the chemicals used for purification, or else later on during the saturation with ammonia. Solvay asserts that the presence of calcium and magnesium salts prevents the complete saturation of brine with NaCl. But it is a fact that, even in the application of previously purified brine, a rather large quantity of solid salt is subsequently added. If an aqueous solution of ammonium carbonate, not previously saturated with NaCl, is employed for purifying the brine, this necessarily involves adding solid salt to compensate for the dilution.

For the comparatively rare case in which brine must be artificially prepared entirely by dissolving solid salt, Solvay recommends the following apparatus:—

A low tank, made of iron, wood, or stone, divided by vertical partitions into six or more compartments, each of which communicates with the next one, so that the water entering into the first travels along in a serpentine course to the last, is filled with salt; and through an opening just above the bottom in one of the corners water is admitted, which is conveyed by a pipe from the bottom of another tank. The latter is divided into two compartments: water is run into one of these, and flows into the other over the partition, which is of the same height as the partitions in the lixiviating-tank; so that the level of the water in the latter is always the same. The water flowing over into the second compartment of the water-tank runs away through a waste-pipe. On its way through the lixiviating-tank the water is converted into saturated

brine of  $42^{\circ}$  Tw., and in the last compartment is diluted by a jet of water to  $38^{\circ}$  or  $40^{\circ}$  Tw. This is done because from a saturated brine, on admitting  $\text{NH}_3$ , crystals of  $\text{NaCl}$  separate, which are not further acted upon. The last compartment is larger than the others, and contains a filter for retaining the impurities of the brine.

Fig. 1.

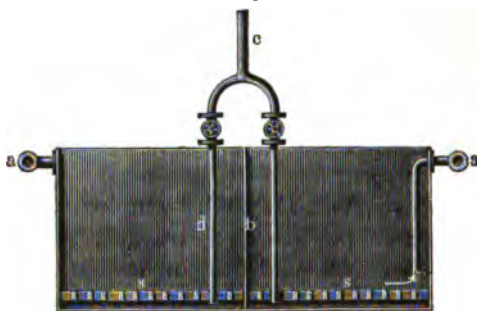
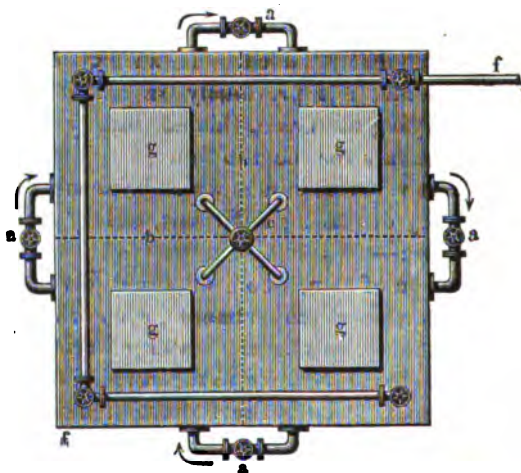


Fig. 2.



A similar apparatus is described by Schreib (Chem. Zg. 1890, p. 490), as shown in figs. 1 and 2. A tank is separated into four compartments by partitions  $b, b$ . The salt is charged through openings  $g, g$ , and rests on the wooden grid  $s$ , covered with rough cloth. Each compartment is supplied through  $f$  with water or dilute brine, circulating by means of the overflows  $a, a$ ; the



saturated brine is taken away by the pipe *c*, from which a branch *d* dips into each compartment underneath the false bottom, in order to receive only clear liquor. By means of taps, each compartment can be put out of series, or can be put in as the first, second, third, or fourth of the series. If from 0.5 to 1 per cent.  $\text{NH}_3$  is employed for removing the earthy salts, 1 litre of brine will hold from 290 to 300 grams  $\text{NaCl}$ .

Before the brine is put into the apparatus for saturating with ammonia, it is partly or entirely employed for *washing the gases escaping into the air* from the saturators and carbonators, to save the ammonia always carried away by these gases. This is sometimes done by means of large apparatus, similar to carbonating-towers. In the case of crude brine there is, of course, a precipitation of calcium or magnesium carbonate, which is removed by settling or continuous decantation (comp. *infra*) before introducing the clear liquor into the saturators. Or else columns are employed like those belonging to the ammonia-stills, in which the brine descends, and the gases to be washed bubble through the brine in many jets in each compartment of the column. This must be effected either by pressure of the gases from below or by suction from above; in the case of the gases from carbonating-towers the former, in those from ammonia saturators the latter is preferable.

## II. Preparation of the Ammoniacal Solution of Salt.

The purified solution of sodium chloride, obtained as above, must now be saturated with ammonia, coming from the ammonia-stills, together with somewhat considerable quantities of carbonic acid, which, however, never suffice to form even normal ammonium carbonate. We first describe the apparatus mentioned by Solvay in his patents of 1872, and shown in fig. 3. *R* and *R'* are tanks for brine; *A* is the dissolver for ammonia, communicating with *R* and *R'* above and below by the cocks *p*, *p'*, *r*, *r'*; only one of the tanks *R* *R'*, alternately, is connected with *A*. Suppose this to be *R*, *p* and *p'* are opened, and  $\text{NH}_3$  gas is admitted through *T*, from the still (comp. Chapter VI.), into *A*, where it is distributed by the perforated false bottom *F* and quickly absorbed by the solution. From *R*, into which a quantity of milk of lime suitable for that special brine has been introduced, and the contents of

which are agitated by  $W W'$ , the brine flows into  $A$  and back  
Fig. 3.

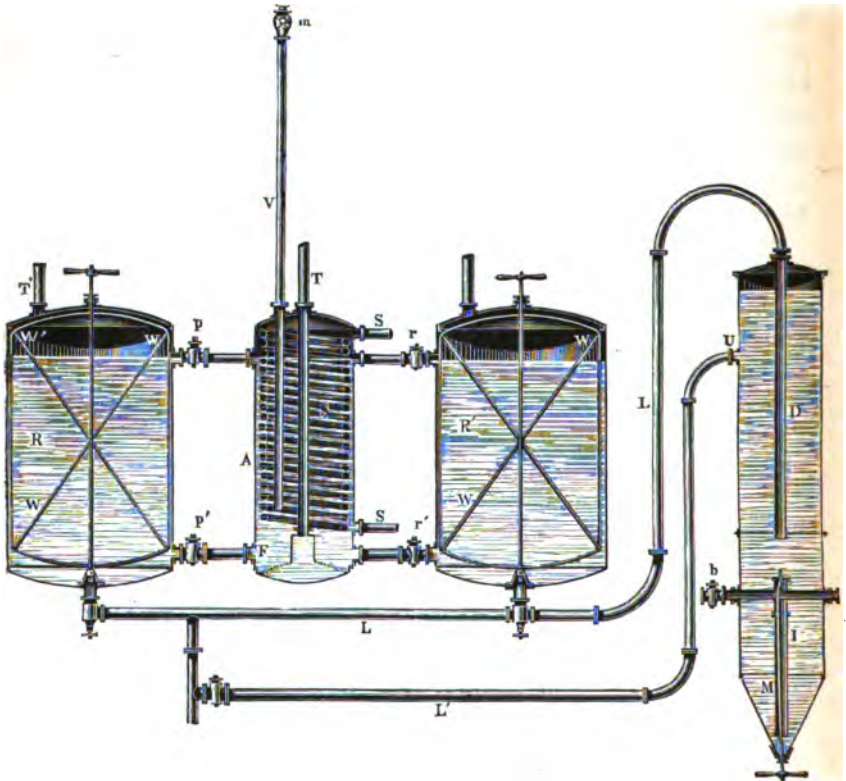
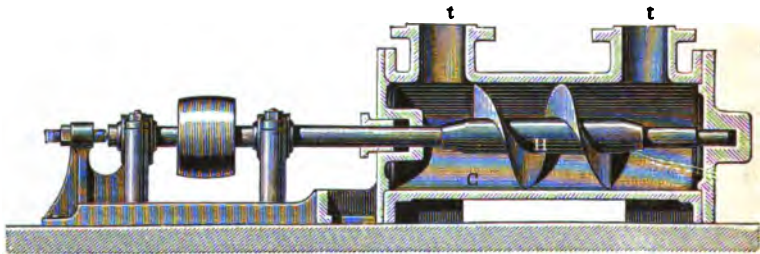


Fig. 4.



again ; the circulation is produced by the agitating arms  $W W'$ , or in case of need by the screw  $H$  (fig. 4) revolving several hundred times per minute and inserted in one of the connecting-pipes between  $R$  and  $A$ . As the temperature rises very much on the

absorption of the ammonia, there is a cooling-worm S placed within the dissolver A, in which water circulates. The pipe V serves for introducing ground salt in case the brine is not strong enough—the proportions being regulated by a wheel divided into several compartments, *m*. T' is a pipe for the escape of air, which, being charged with  $\text{NH}_3$  vapour, is carried into an absorbing-apparatus charged with brine. For the rarer case of a natural brine being too strong, Solvay recommends an automatical diluting-apparatus, in his patent No. 999, 1876.

The saturation of brine with ammonia must be carried to a certain point, which can be recognized by the brine, its volume being increased by saturation with  $\text{NH}_3$ , attaining a certain level. This can be tested by hand, and the position of the cocks altered accordingly; but of course an automatic arrangement is preferable. In 1863 Solvay availed himself for this purpose of the difference in specific gravity between the pure brine ( $38^\circ$ – $40^\circ$  Tw.) and that saturated with ammonia ( $30^\circ$ – $25^\circ$  Tw.). Following the law of communicating tubes, the brine saturated with ammonia rises to a greater height, in order to balance the pure brine; and it was only necessary to put a lateral pipe for running away the liquor, to which it must rise when its specific gravity has sunk down to  $25^\circ$  Tw. This principle could not be applied when Solvay introduced large and varying quantities of carbonic acid at this stage of the process; by this the bulk of the liquid is increased but very little, its density very much. Hence he employed later on an automatic apparatus based entirely upon the increase of volume of the brine on saturation with  $\text{NH}_3$ , and independently of the  $\text{CO}_2$ . The dissolver for ammonia is connected with two reservoirs, one of which measures the brine and introduces it into the dissolver, whilst the other draws off a corresponding quantity of ammoniacal brine when it is sufficiently saturated. This is done by means of a float in one of the reservoirs, which, when the ammoniacal brine has risen to the proper level, opens a valve by means of a lever arrangement and allows the brine to run out, whereupon, as it descends, another valve is opened, by which the requisite quantity of fresh brine is again introduced.

It would appear that this automatic saturating-apparatus, even in its new form, was not altogether satisfactory: it is very ingenious; but the play of valves and levers is somewhat complicated. At least it was not employed at Northwich on my visit in 1878, but

the degree of saturation of the brine with ammonia was found by titrating, as usual everywhere else. We accordingly refer for the drawing and detailed description of the apparatus to the patent-specification (No. 1904, 1876, p. 11). In practice not two, but a larger number of dissolvers for ammoniacal brine are combined to form a set.

When the brine contains enough ammonia, the agitator in R (fig. 3) is stopped; any precipitated magnesium or calcium carbonate, along with insoluble impurities of freshly dissolved salt, quickly settles down, and can be drawn off at the bottom, where the vessels are made conical and provided with mud-valves. Where large quantities of mud have to be dealt with, Solvay employs the continuous decanting-apparatus D (fig. 3). The mud, of course mixed with a good deal of liquor, is forced by means of compressed air or carbonic acid, acting upon the surface of the liquid in R, through the pipe L into the tall cylinder D; the liquid from this overflows through U; the mud remains lying in the conical bottom, from which it is scraped off by the scraper M; it again rises in the pipe I, and is run off through *b*. According to requirements, more or less of the contents of R are passed through the decanting-apparatus. Another, similar apparatus is described in the patent No. 999, 1876, p. 4.

After decantation the ammoniacal brine is filtered, in order to be obtained perfectly clear; otherwise all its impurities would pass over into the soda. Since the particles still suspended are very fine, a closely-woven cloth must be employed for filtering; and this necessitates strong pressure, which is effected by the cylinder B (fig. 11, p. 34), within which a smaller cylinder O, with many perforations, is fixed. The filtering-bag is either inside O, and consequently taken out when full of mud; or it is outside, in which case the mud is removed by *d*.

In lieu of decanting-apparatus, filter-presses are frequently employed for this mud.

Instead of the complicated apparatus described in Solvay's patents, others employ plain cast-iron cylinders, at the bottom of which there are inlets for fresh brine and for ammonia-gas, regulated in such quantity that a sufficiently strong solution is formed; this at the top runs by means of an overflow into storage-vessels, which may be made to act as settlers. The inner worm, shown in fig. 3 at S, is, I am informed, left out even at the

Solvay works, as it quickly becomes blocked with crusts, and the cooling is all done from without. It is necessary always to keep the temperature below  $70^{\circ}$  C., to prevent decomposition of ammonium carbonate. An excessively low temperature is injurious in the case of imperfectly purified brine, as it prevents the precipitation of calcium carbonate in crystalline form.

Another kind of cooling is said to be both simpler and more efficient, viz., adding some ammoniacal brine obtained in a previous operation, and cooled in the manner to be described below.

The vessels R R', fig. 3, have been recently abolished in the Solvay works, so that there is little left of the ingenious but complicated apparatus of 1872, and practically the same simple apparatus is employed as is used by most other manufacturers. But the continuous decanting-apparatus, shown in fig. 3 at D, has answered very well; three such are employed in succession, and they suffice without the filters B, shown in fig. 11, which had to be done away with, as they were constantly stopped up.

A large number of special apparatus for the preparation of ammoniacal salt solution is described in many patents, partly embracing mechanical stirring, and mostly connected with special carbonating apparatus; for this reason we must refer to the enumeration given in the next chapter. We have already remarked that no complicated apparatus is needed for this part of the process.

Boulouvard's dissolving apparatus is intended to prepare from solid salt at once an ammoniacal brine, by dissolving the salt in the ammoniacal solution obtained in regeneration of ammonia, containing more or less  $\text{CO}_2$ . In figs. 5 and 6, A and A' are two tanks filled with ammonia-water. As the strength of this liquor varies, it is brought to the proper strength of 900 grams per litre (?) by either adding water or stronger liquor. By opening one of the taps *c, d, e, f*, communication is made with the salt-boxes B, B', which are always kept full from above. The ammoniacal liquor running in forms an ammoniacal brine, at the same time lowering the temperature; this liquor is filtered through the sieves *g, g*, and is pumped away to the carbonators. The covers are made tight by india-rubber washers and screws. All communications with the air are provided with scrubbers for retaining any  $\text{NH}_3$  escaping (p. 25).

Fig. 5.

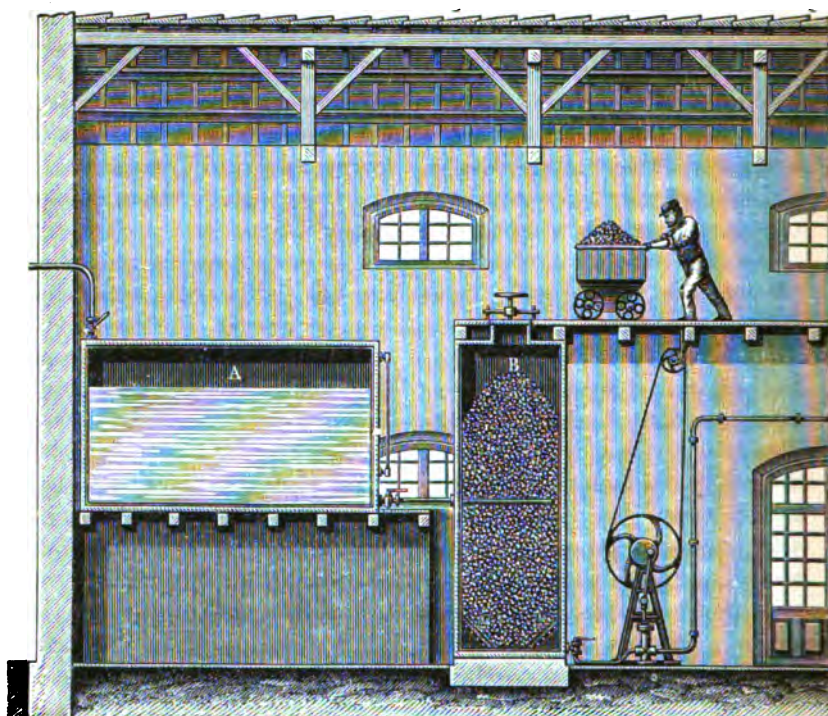
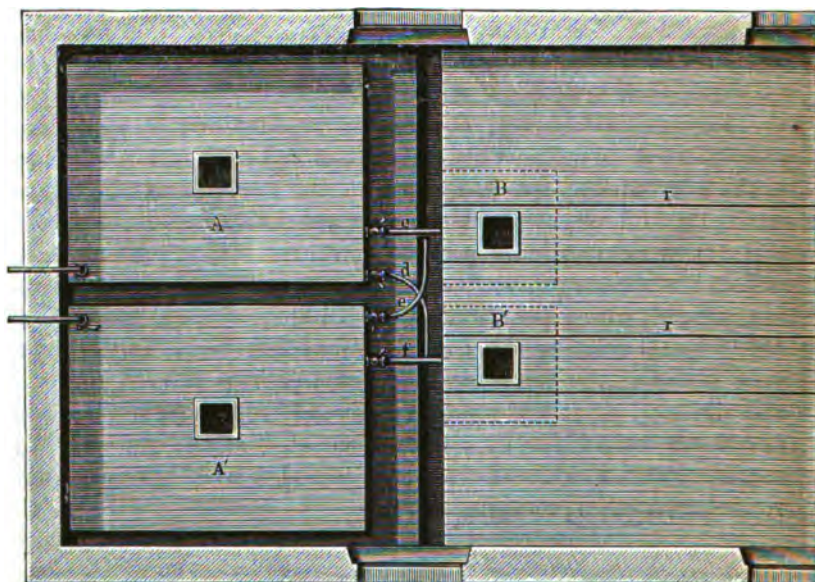


Fig. 6.

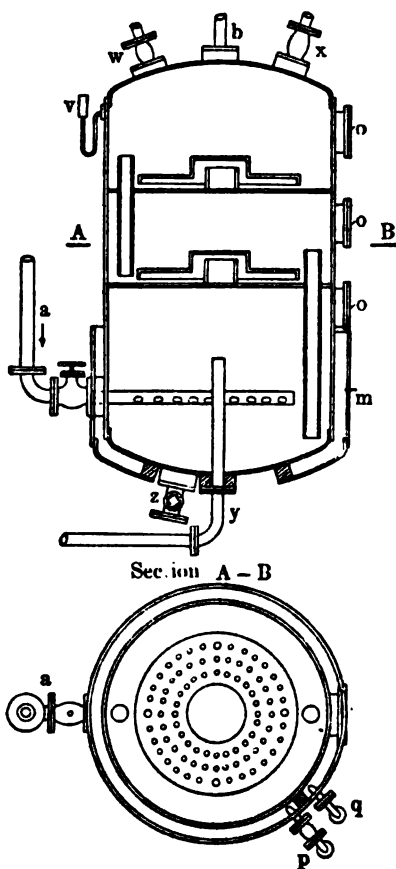


According to Landolt's report, in Hofmann's Vienna Exhibition Report, i. p. 452, Honigmann also dissolved rock-salt in aqueous ammonia, leaving behind the soluble impurities. Later on, Honigmann abandoned this process, and saturated his brine (22° Baumé) and the dissolving vessel itself up to 18 per cent.  $\text{NH}_4\text{Cl}$ . These vessels have conical bottoms, from which the mud is from time to time removed.

Fassbender describes the following apparatus, shown in figs. 7 & 8, constructed on the principle of a "column." The lower portion of the column is surrounded with a cold-water jacket, *m*, with inlet and outlet *p* and *q* for the cooling-water. The ammonia-gas enters at *a*, the unabsorbed gas escapes at *b*; *x* is the inlet for brine, *y* the outlet for the same, *z* the discharge-pipe for the bottom compartment, *o, o* manholes; besides which each column has three pet-cocks for taking samples and gauging the depth of liquor. The top compartment bears a pressure-gauge, a vacuum-gauge *v*, and water-pipe *w*. The non-absorbed gases are taken away through *b* by a vacuum-pump, and forced through the same scrubber which serves for the exit gas from the carbonators. From this they pass through an acid washer and thus into the open air.

When passing dry ammonia-gas into saturated brine, salt would be precipitated, as  $\text{NaCl}$  becomes less soluble with increasing percentage of ammonia (p. 15). But in reality the ammonia frequently arrives from the stills pretty well charged with moisture,

Figs. 7 &amp; 8.





in spite of cooling, and this dilutes the brine, which therefore can take up more salt after being saturated. This fresh salt can be put in the top part of the carbonating-tower (as prescribed by Solvay), or immediately below the top; or else the ammoniacal brine is run through a box filled with salt, and only then into the well from which it is pumped into the carbonators.

The saturation with ammonia is usually carried so far that the liquor titrates from 60 to 70 grams  $\text{NH}_3$  per litre; the original bulk of the brine is then increased by 9 per cent. Of this percentage only 60 grams per litre are left in the Solvay towers, as these receive some fresh brine at the top for washing the gas (see below). We have seen on p. 16 how far the transformation of the  $\text{NaCl}$  is influenced by the saturation with  $\text{NH}_3$ . 70 grams  $\text{NH}_3$  per litre is rarely exceeded, as this causes inconvenience by stopping up the pipes with ammonium carbonate; usually the strength is rather below 70 grams. Schreib (Chem. Zg. 1890, p. 491) considers 65 grams  $\text{NH}_3$  and about 270 grams  $\text{NaCl}$  as the best strength. In a special case known to me, the average was 62 grams  $\text{NH}_3$ .

The *testing of the ammoniacal brine* is carried out as follows:—Sodium chloride is tested by neutralizing with nitric acid (the reaction must be exactly neutral or slightly alkaline, but not acid), then adding a little potassium chromate and titrating with standard silver solution up to a red colour. 1 c. c. of a decinormal solution shows 0.00585 gram  $\text{NaCl}$ ; but it is usual to employ a special solution, *e. g.* one containing 2.906 grams  $\text{AgNO}_3$  per litre, indicating 0.001 gram  $\text{NaCl}$  per c. c. The number of c. c. of the standard solution used must be diminished by 0.2, to allow for the production of a sensible red tint of the  $\text{AgCl}$ .

Ammonia is tested sometimes by directly titrating with standard acid; but as there is also chloride and sulphate to be considered, it is better to dilute 10 c. c. to 100 c. c. and boil in a flask, absorb the  $\text{NH}_3$  expelled in standard acid, and re-titrate with standard soda solution. After this has been done, the receiver is again charged with standard acid, caustic soda solution is run into the flask by a funnel-tap, and the fixed ammonia estimated in the same way as described in the 6th chapter in connection with gas-liquor.

A simpler way of proceeding is this: estimate the caustic ammonia and ammonium carbonate by direct titration with



standard acid and methyl-orange, the total ammonia by distilling with caustic soda, and the fixed ammonia by subtracting the former from the latter.

The  $\text{NH}_3$  absorbed by brine in the scrubbers is estimated by direct titration with acid.

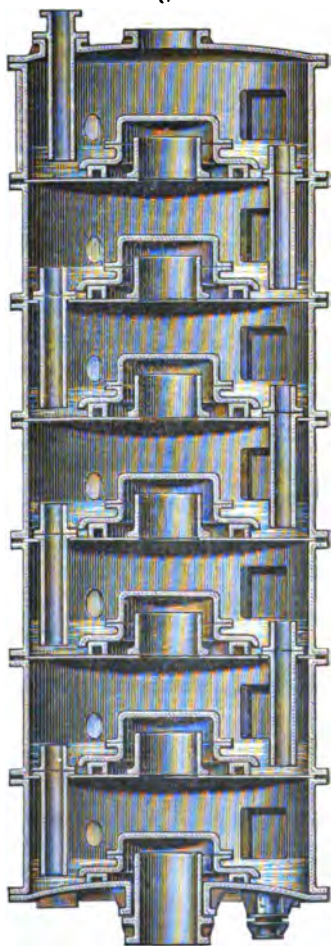
*Washing the Exit Gases.*—We know that the saturators never communicate freely with the atmosphere, which would cause a large loss of ammonia; but there are always washers (scrubbers) interposed in which the  $\text{NH}_3$  is retained by water, or better by brine. It is considered a special advantage (and is carried out at the best works) not to work the washers under pressure, but, on the contrary, to *aspirate* the air from the ammonia-saturators and through the washers, which must be made amply large. Since the saturators communicate directly with the ammonia-stills, the latter also work with a slight underpressure, or at least without any outward pressure, which both prevents any leakage of ammonia without and causes the ammonia to be given off much more easily.

A washer suitable for the application of a vacuum is shown in fig. 9.

*Pumping the Brine.*—This is generally done by means of compressed lime-kiln gas, a branch from the gas-main being provided for this purpose.

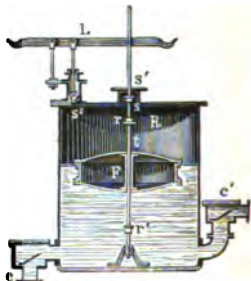
A self-acting pressure-apparatus, invented by Solvay, which at the same time serves for measuring the liquid, is represented in fig. 10. The liquid flows through the valve-box *c* into the vessel *B*; with this the float *F* rises until it touches the washer *r* fixed upon the rod *t*, which it raises, and with it the valve *s*, by which

Fig. 9.



the opening  $s'$  is closed.  $t$  also acts upon the lever  $L$ , which raises the valve  $s^2$  and admits into the apparatus compressed air or gas, which forces out the liquid through the valve-box  $c'$ . The float  $F$  descends with the liquid till it comes into contact with the washer  $r'$ , and draws down the rod  $t$ , which stops the admission of compressed gas and opens the valve  $s$  for the escape of compressed gas through  $s'$ . Fresh liquid then enters through  $c$ , and the operation begins again. An ordinary meter attached to the lever  $L$  indicates the number of times the lever has been worked, and with it the volume of the liquid forced. This apparatus works very well, and was in constant use during my visit in 1878.

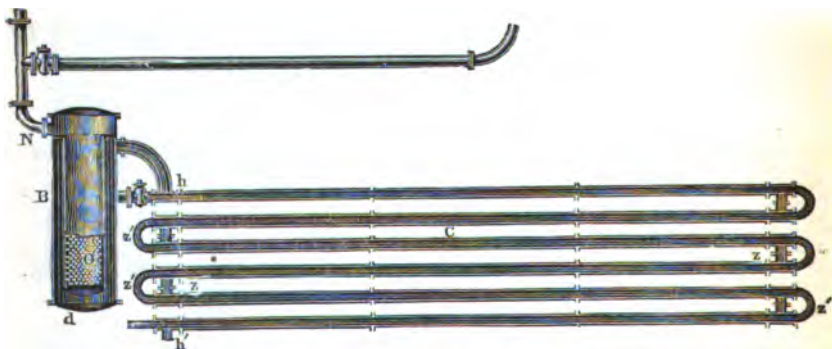
Fig. 10.



### III. *Cooling of the Ammoniacal Salt Solution.*

The perfectly clear ammoniacal brine must now be cooled down very much before being treated with carbonic acid. This is done, in addition to the preliminary cooling by the refrigerating-

Fig. 11.



coil  $S$  in the cylinder  $A$  (fig. 3), by means of a cooling-apparatus  $C$  (fig. 11), composed of concentric tubes, like a Liebig's cooler. The inner tubes communicate alternately at their ends by bends  $z'$ ; the outer pipes also alternately at both ends by the straight pipes  $z$ . The best way is to run the cooling-water in the inner tube  $z'$ , and the brine in the annular space, so that it enters through  $h$  and leaves through  $h'$ ; it can thus be cooled once more by water

running outside all over the apparatus. The cooler need not be placed below the dissolver A, but may be alongside of it, since the liquids have, in any case, to be forced onward by compressed air or carbonic acid.

The pipes must be constantly tested for their tight state, by trying for  $\text{NH}_3$  in the cooling-water with Nessler's reagent.

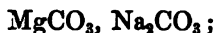
It appears that recently the Solvay works have abandoned the former constructions patented by Solvay, and have returned to plain pipe-coolers, without inner pipes, consisting of 20 superposed tiers of 9 pipes each on the horizontal plane; in these the ammoniacal brine travels from the bottom upwards, the whole system being cooled by a stream of water running down on the outside.

Fassbender (comp. p. 31) calculates the cooling surface for ammoniacal brine required for producing 10 tons of soda-ash per 24 hours at 70 square feet, assuming a maximum temperature of  $43^\circ \text{C}$ . for the liquid and  $20^\circ \text{C}$ . for the cooling-water, with a consumption of 8 tons of water per hour.

Sometimes very troublesome *crusts* are formed in these coolers, up to 4 inches thick. Reinitzer (Zsch. f. angew. Ch. 1893, p. 446) found such crusts composed according to the formula



Very similar crusts had been previously observed by Leighton (Chemical News, lvii. p. 3), and by Cooke in 1886. Pennock subsequently found crusts corresponding to the formula



these had been formed at somewhat lower temperatures (Chem. Trade Journal, 1893, xii. p. 191). Although there was but very little magnesia in the brine (which contained 4.54 grams  $\text{CaSO}_4$ , 2.14  $\text{CaCl}_2$ , 0.586  $\text{MgCl}_2$ , 290.0  $\text{NaCl}$  per litre), crusts  $\frac{3}{4}$  inch thick were formed in four months.

This shows that the magnesia should be removed as thoroughly as possible before the brine enters the saturator.

## CHAPTER III.

## PRODUCTION OF CARBONIC ACID.

*Lime-kilns.*

THE carbonic acid required in the ammonia-soda manufacture is obtained from two sources:—in the first place, from the conversion of the bicarbonate into monocarbonate: this, theoretically, would yield half the  $\text{CO}_2$  required; but since the  $\text{CO}_2$  of the bicarbonate cannot be recovered completely, the much larger portion of carbonic acid must be procured in another way, which is at once afforded by the burning of the lime required for recovering the ammonia.

The *lime-kilns* are of the usual upright kind, contracted at the bottom part, with an iron shell. They were formerly built with lateral fire-places, so that only the flame proceeding from the fuel came into contact with the limestone. This kind of kiln, which is frequently used for the production of lime for building-purposes and for that of  $\text{CO}_2$  in sugar-works, has not been found to answer for the present purpose, where the gas must contain the greatest possible amount of  $\text{CO}_2$ . It has been universally preferred to return to the old plan of burning the lime by charging the limestone *mixed with coke* (bituminous coal is entirely excluded here). In this case the fuel is more completely utilized, and consequently the gas is richer in  $\text{CO}_2$  than with less favourable combustion. Of course such plain kilns are cheaper to build, to keep in repair, and to work than more complicated forms. The only drawback is that the ashes of the fuel remain mixed with the quicklime; but this is of no consequence, as the lime is used up on the spot, and anything remaining for sale can easily be picked clean.

Annular kilns do not appear to be adapted for this purpose; but this is probably not the case with the Dietzsch kiln, which has proved a great success in the manufacture of Portland cement.

The *limestone* employed should be of good quality. In many localities it can be procured containing 98 per cent.  $\text{CaCO}_3$ , and yielding 95 per cent.  $\text{CaO}$ . A supply of good and cheap limestone is an important factor when planning an ammonia-soda works. Some analyses of limestone are given in Vol. II. p. 486. The chemical analysis is generally very simplified in this case. Generally it is only tested for what is insoluble in dilute hydrochloric acid and for calcium carbonate, the latter most conveniently and quickly in Lunge and Marchlewski's gas-volumetric apparatus, Vol. II. p. 113; or else alkalimetrically by dissolving 1 gram limestone in 25 c. c. standard hydrochloric acid, and retitrating with standard soda solution. If  $n$  c. c. of the latter have been used,  $5(25-n)$  indicates the percentage of  $\text{CaCO}_3$ . Any magnesia present is in this case calculated as lime; but this is quite admissible in the present case, more particularly as very little of it occurs in ordinary limestone, and magnesian limestone is not applicable for this industry.

The *quantity of coke* to be charged with the limestone necessarily depends in the first place on its quality, but, apart from this, varies greatly in different works. Schreib (Chem. Zg. 1890, p. 490) quotes 28 coke for 100 quicklime with long-flame kilns, or 22 coke when directly charged with the limestone, the latter yielding better gases. Others charge from 12 to 14 coke for each 100 of raw limestone, which amounts much to the same thing. In the cost accounts to be quoted later on much more coke is mentioned, but this is probably owing to its being partly intended for use in calcining the soda.

In a more recent publication (Chem. Zg. 1894, p. 1947), Schreib gives much lower figures, viz., from 15 to at most 20 parts coke for 100 quicklime, equal to 8.4 to 11.2 coke for 100 limestone. The lower of these values so nearly approaches the theoretical minimum of 13.1 coke for 100  $\text{CaO}$ , calculated by himself, that it seems doubtful whether it is practically attainable.

The coke is, of course, all the better the less ashes and sulphur it contains. Oven-coke is in this case less suitable than gas-coke, which is more porous and much cheaper.

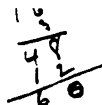
Theoretically 106 parts of pure sodium carbonate require the  $\text{CO}_2$ , and the  $\text{CaO}$  of 100  $\text{CaCO}_3$ , or 100 parts 98 per cent. soda-ash require about 100 parts good limestone. This supposes that all the

$\text{CO}_2$  evolved in calcining the bicarbonate returns into the process, that the  $\text{CO}_2$  in the carbonators is entirely used up, and that the ammonium chloride is decomposed by the theoretical quantity of lime; also that the  $\text{CaCO}_3$  is completely split up into  $\text{CaO}$  and  $\text{CO}_2$ . None of these suppositions is practically realized or nearly so. Under all circumstances much more limestone is consumed than the weight of the alkali produced. Since the recovery and utilization of the  $\text{CO}_2$  is even less complete than the action of the  $\text{CaO}$  in decomposing the  $\text{NH}_4\text{Cl}$ , as a rule considerably more lime must be burnt in order to obtain the requisite amount of  $\text{CO}_2$  than is required for recovering the ammonia. This excess of lime is easily used up, where caustic soda is manufactured, otherwise it must be utilized in a different way.

The quantity of limestone consumed for 100 parts of soda-ash is very differently stated in the cost accounts quoted later on. Schreib, in 1890, stated it = 200 to 250 parts. In 1892 he stated it as 150 to 190, or on an average 170 parts. I can confirm from a thoroughly reliable source that 170 parts suffices in well-conducted factories, but this amount is frequently very much exceeded. From the analyses of the waste liquor at La Madeleine, to be quoted hereafter, we may conclude that they there ran to waste, on an average, 25 calcium hydrate (=  $33.8 \text{ CaCO}_3$ ) and 5  $\text{CaCO}_3$  for each 25  $\text{CaCl}_2$  (=  $22.5 \text{ CaCO}_3$ ); they thus lost 38.8 limestone for each 22.5  $\text{CaCO}_3$  utilized, and they must have consumed 270 limestone for 100 soda-ash, in lieu of 100 limestone! It is true that those analyses (by Jurisch) do not inspire much confidence, but at all events the waste must have been very great there. But I have ceased to rely on such statements as this which I have met with: that 100 soda can be made with 60 lime = 107 limestone, for this is too near the theoretical limit. We may state now (1894) a consumption of 120 to 130 limestone to be *exceptionally* good, and 150 to 170 as being the average.

If the lime-kilns supply occasionally or on the average more carbonic acid than is required in the manufacture and taken away by the air-pumps, the excess is allowed to escape into the air by an open pipe. There is no fear of air being drawn in through this pipe, as there is always a certain outward pressure in it.

In order to obtain gas containing at least 30 per cent.  $\text{CO}_2$ , as is highly desirable for this manufacture, in the first instance the kilns are made very large, so that the oxygen of the air is



completely utilized. The best size is from 33 to 40 feet high or even more, and 7 to 10 feet wide inside, with a minimum consumption of 15 tons limestone per day. Care must also be taken that the coke is completely consumed before the charges arrive at the discharging-holes at the bottom, so that the lower part of the kiln is cold.

In the case of very tall kilns, the upper part is not so hot as the lower portion, because the oxygen of the air is already used up and the coke cannot take fire; the heat of the gases is therefore partly spent in heating up the charges, which both causes a saving of fuel and less dilution of the gas given off by the limestone with the products of the combustion. Of course this must not go so far that carbon monoxide is formed. The materials should be charged as dry as possible, so as to reduce the consumption of fuel and increase the richness of the gas.

In consequence of no extra fire-places being provided, the work is simpler and repairs are slight. With such large kilns the gas is not merely richer in carbonic acid, through the complete consumption of the atmospheric oxygen, but its composition is more uniform, in spite of the inevitable disturbance in charging and discharging.

Lime-kilns serving for our purpose must have a closed top, and one or more gas-outlets below the cover. The limestone is charged through man-holes at the top, with well-fitting covers. The shape of such a kiln will be understood from figs. 12 to 15. *a* is the man-hole cover with its lever (enlarged in figs. 14 & 15); *b, b* the outlets for gas which collects in the annular channel *c, c*, and is carried away by pipe *d*; *e, e* discharging-holes for quicklime, of the older, simple kind.

Private communications from Mr. H. Schreib give the subjoined information on lime-kilns used by himself. Fig. 16 represents a kiln 33 feet high, 9 feet 4 inches inside diameter at the wider part, and 6 feet at the mouth, with a charging-hole 2 feet 8 inches wide, an iron shell  $\frac{3}{4}$  inch thick, an insulating layer of 4 inches, and a fire-brick lining 15 inches thick. It furnishes in 24 hours from 11 to 13 tons quicklime, according to the quality of the limestone. Coarse-grained limestones, containing 98 per cent.  $\text{CaCO}_3$ , are best to burn, some of them even in large lumps; poorer stone requires more coke and yields poorer gas. Some stones burst in the kilns with a loud report and cause obstructions: these can only be

Fig. 12.

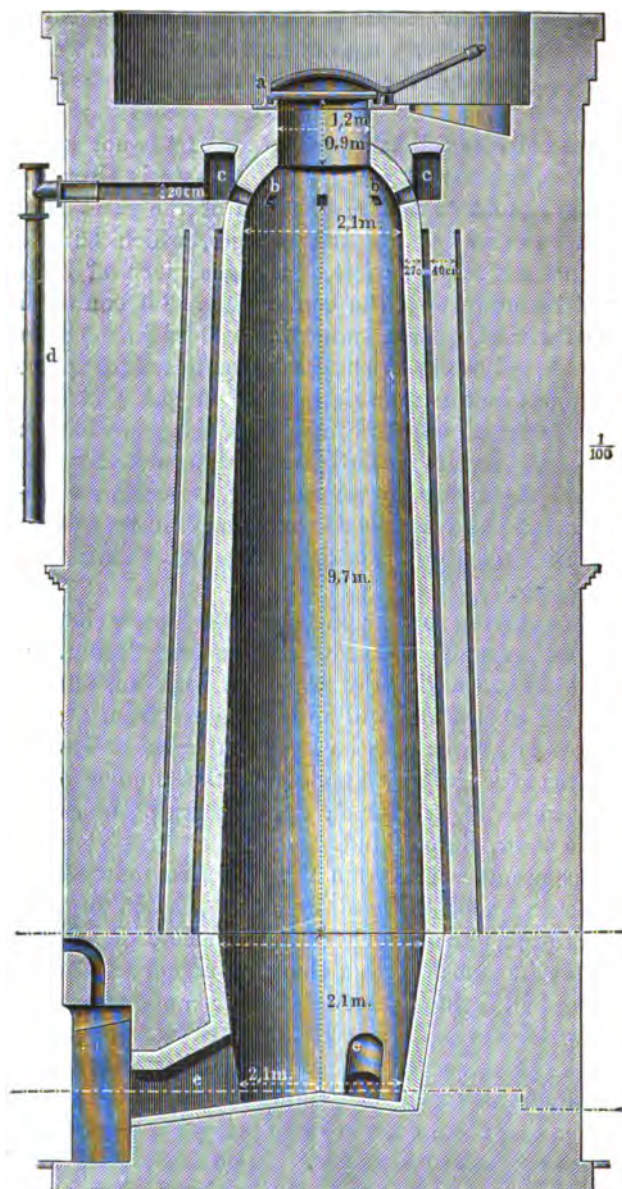




Fig. 13.

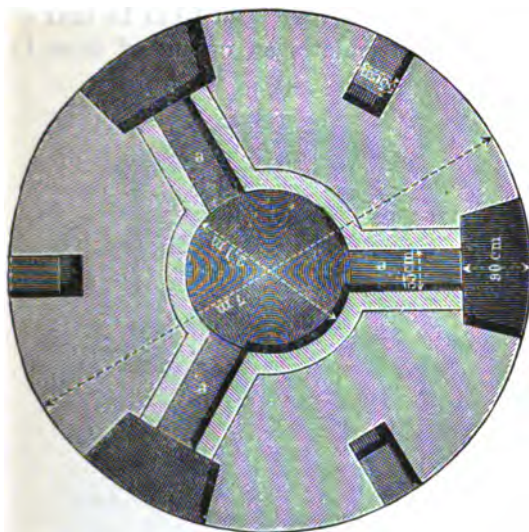


Fig. 14.

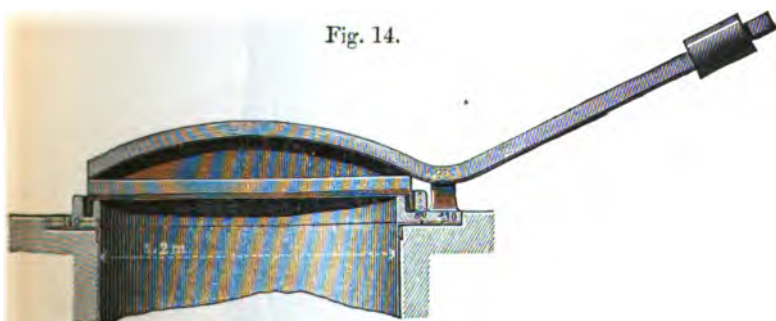
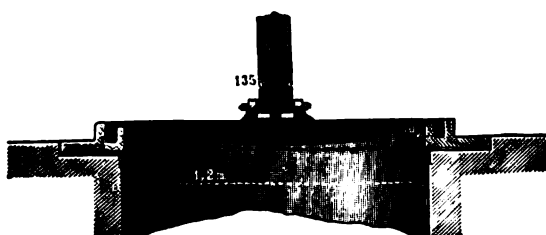


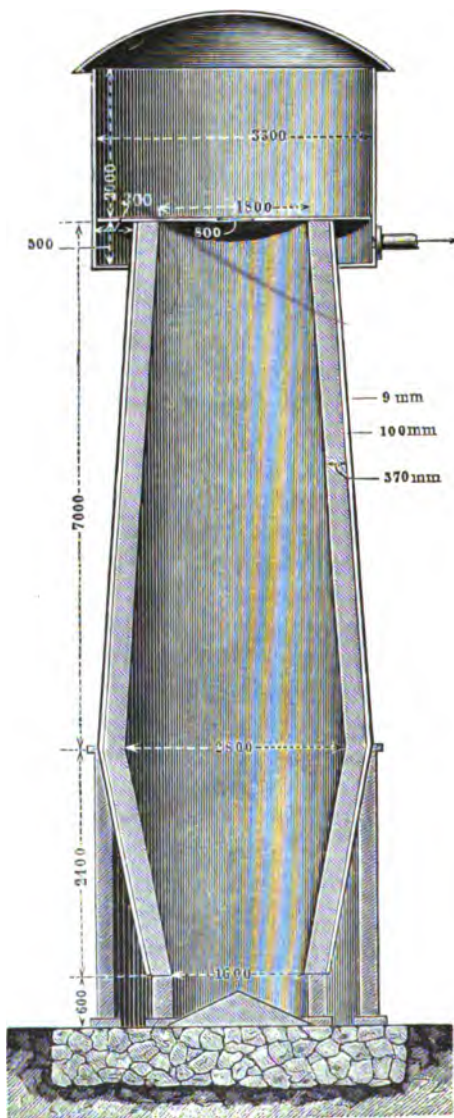
Fig. 15.



burnt in periodically and slowly worked kilns, and are therefore useless for our purpose.

In the case of kilns supplying from 10 to 15 tons of quicklime in 24 hours, Schreib calculates an output of from 15 to 22 lbs.

Fig. 16.



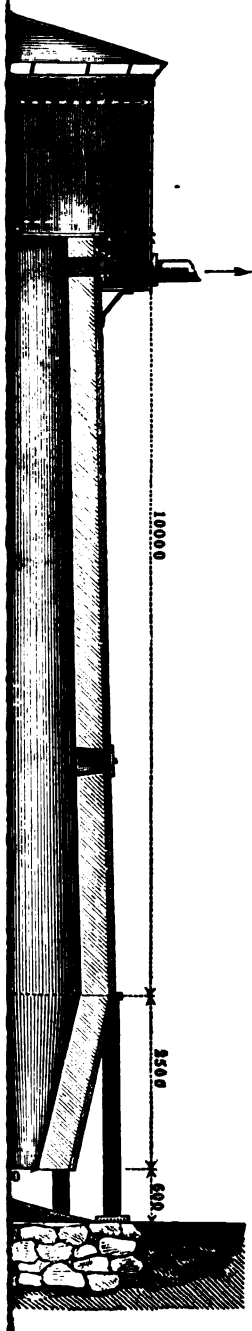
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[*Lunge*, vol. iii.]



quicklime during 24 hours per cubic foot of the total kiln space, or from 19 to 25 lbs. per cubic foot of the available cubic space.

The shape shown in fig. 17 furnishes about as much work as the former, but it is narrower (7 feet inside diameter in the widest parts) and higher (43 feet). Such kilns have proved very successful, and with these the consumption of coke has been reduced to from 18 to 20 parts for 100 quicklime; whereas the kilns with side fires, formerly used in the same place, required from 25 to 30 parts of coke. With large kilns, furnishing from 15 to 20 tons  $\text{CaO}$  per day, it is possible to go down to as little as 16 coke for 100 lime, on the supposition of careful work and constant analytical control, to prevent the presence of either oxygen or carbon monoxide in the gas. The men obtain a good idea of the process by watching the heat through peep-holes in the sides of the kiln.

The charging is most conveniently performed by first tipping a barrow-load of coke, and then from 5 to 7 barrow-loads of limestone. The quicklime is best drawn out at the bottom almost continuously, in order to obtain gas of high and regular strength. This is easier with the high shape, fig. 17.

Both shapes must be provided with a chimney, to produce draught during the stoppages of the pump.

The discharging of the quicklime is most conveniently performed where the bottom of the kiln is provided with a large grate, on which the whole contents of the kiln are supported, and by the shaking of which the bottom portions, which are burnt out, fall down into the ash-pit, through which at the same time the necessary air is admitted. This can be done almost continuously with large kilns. A grate, indeed, is not absolutely required, the bottom layer of quicklime serving as such, but a real iron grate is preferable, as it is then possible to run an iron barrow on rails underneath the grate and to drop the lime directly into this.

In any case the kiln proper rests on short cast-iron columns and girders, like a blast-furnace, so that the space below is accessible.

Solvay (Engl. pat. 13322, 1887) describes a lime-kiln provided with an air-blast and a mechanical discharging arrangement.

The minimum percentage of  $\text{CO}_2$  in the gas in the case of large kilns is 30 per cent., but it may rise to 32 per cent. Sometimes practical men assert that they get gas of 35 per cent. and upwards. This is, however, probably deceptive, and may be caused by

$\text{molar mass} = 2a + c$   
 $\text{atomic n}^{\circ} = a = 40$   $\text{CaCO}_3$   
 $c = 12$   $40 + 12 + 48 = 100$   
 $O = 16$

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$\text{molar mass} = 2a + c$   
 $\text{atomic n}^{\circ} = a = 40$   $\text{CaCO}_3$   
 $c = 12$   $40 + 12 + 48 = 100$   
 $O = 16$

32  
12  
44

estimation of  $\text{CO}_2$ , which can be done in any of the multifarious gas-burettes or other apparatus for technical gas-analysis, also in the oldest of these, *Winkler's* gas-burette. This simple operation is described in all text-books.

If sulphurous acid is to be estimated as well, this must be done in a separate sample, by treating it with iodine solution, either according to the general methods of technical gas-analysis or by *Reich's* method, Vol. I. p. 324.

The *quicklime* is mostly employed for recovering the ammonia from the mother liquor in the manner to be described in Chap. VI. Where caustic soda is manufactured, it is used for this purpose as well. Its analysis is confined to the estimation of free  $\text{CaO}$  by titrating with standard oxalic acid and phenolphthalein to the point where the pink colour is discharged, and to that of the  $\text{CO}_2$  present, either by the gas-volumetric method (comp. p. 37) or by the difference between the titration with oxalic acid and that with an excess of standard hydrochloric acid, and re-titration with caustic-soda solution: details, Vol. II. p. 744. With good burning the  $\text{CO}_2$  can be reduced to 1 or 2 per cent.

The sampling must be done sufficiently quick to prevent the absorption of carbonic acid and moisture from the air; the large sample must be quickly broken up and mixed, to obtain the small sample for analysis, which must be kept in well-corked tubes.

### *Washing the Lime-kiln Gas.*

The gases taken away from the lime-kilns must be cooled and washed, and that under all circumstances before they enter the air-pump, to prevent any damage to this. The washing must both mechanically remove the large quantity of dust carried away from the kiln, and must also retain the  $\text{SO}_2$  originating from the coke as much as possible; it must also assist in the cooling.

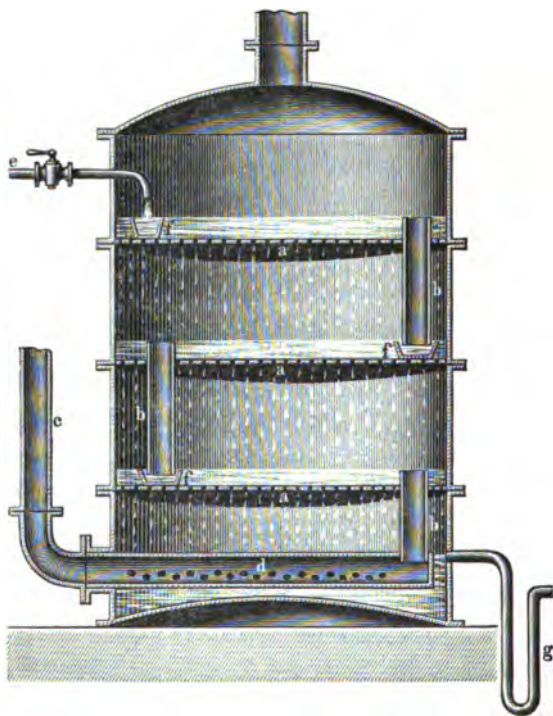
According to my experience, the dust is best kept back by forcing the gas to bubble through a column of water, which need not be deeper than  $2\frac{1}{2}$  inches.

Fig. 18 shows a washer, consisting of a cylinder with three horizontal perforated partitions *a, a*, provided with overflows *b, b*. The gas arrives through pipe *c*, divides itself among the holes of *d*, and rises through those of the partitions *a, a*. The water arrives through *e*, runs into the basin *f*, and from this onto the top partition *a*; part of it then descends in the shape of drops from the

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holes, another part by the overflow, from one partition to the other, and at last issues at *g*. A column of water of a certain

Fig. 18.

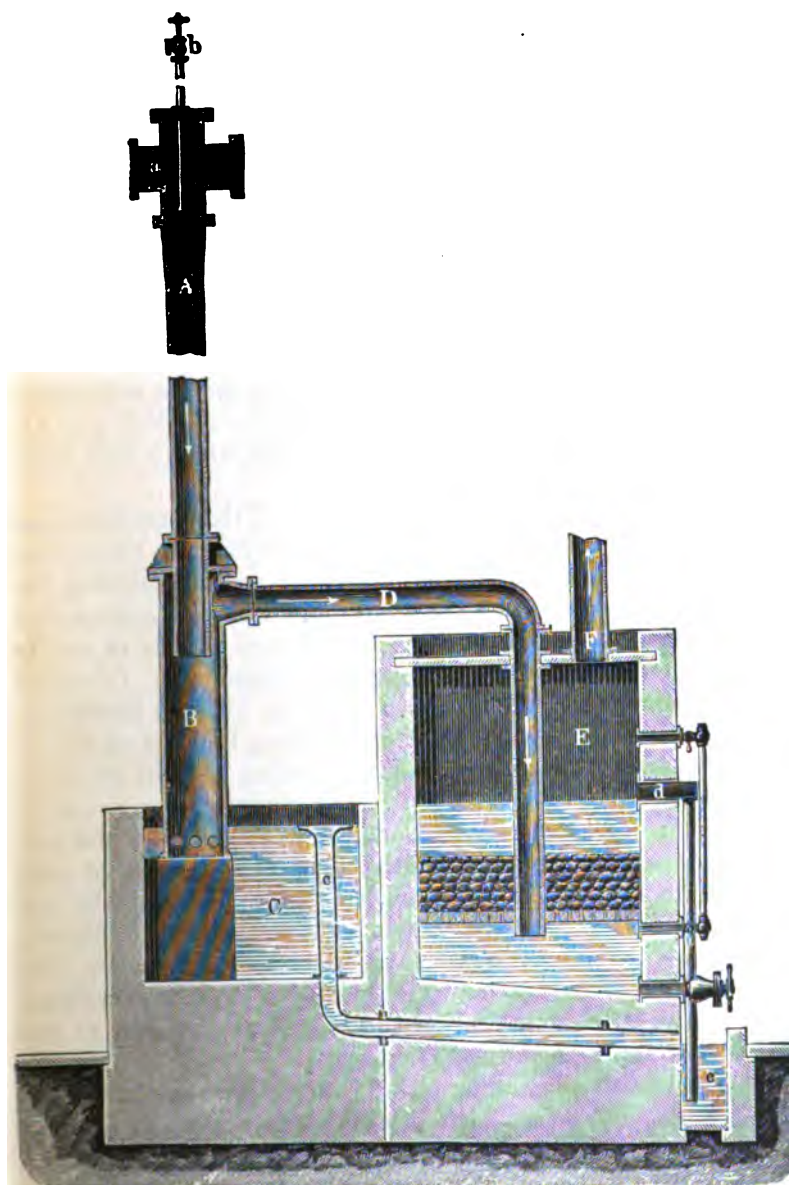


height is kept on each partition by the pressure of the gas issuing from below, so that the gas must bubble through the water and give up both the dust and the  $\text{SO}_2$ .

Another washer is shown in fig. 19. In the long injection-tube *A*, a rose *b* is placed. *A* is continued at the bottom into the bell *B*, provided with larger holes, from which the injected water runs into the vessel *C*, with an overflow *d*, whilst the gas enters through *D* into *E*. Here it must pass a layer of limestone, supported on a false bottom, to better retain the  $\text{SO}_2$ . Here also water constantly enters and runs out again into spout *e* by the overflow *d*. The washer-gas passes on through *F*.



Fig. 10.



*Air-pumps.*

The pumping of the gas from the kilns and into the carbonators is performed by apparatus of very different kind, according to the pressure to be overcome. The high Solvay towers require powerful *blowing-engines*, similar to those employed for blast-furnaces, but adapted to much greater pressure. They were formerly constructed for wet work, especially by English engineering works, and consequently suffered a good deal by the small quantity of sulphurous acid unavoidably remaining in the gas. This is hardly felt in the air-compressors made by Burckhardt & Co., of Basel, which work dry and very economically, by reducing the dead space to a minimum.

The compression of the gas in the blowing-engines evolves much heat, which must be carried away by causing the gas, as it comes from the compressor, to pass through cylinders in which water is injected; the water is separated from the gas, which is now ready for the carbonators or other uses.

Solvay proposed to perform the cooling of the compressed gas partly by its re-expansion, which is to be utilized as mechanical work, by combining with the air-cylinder another cylinder, the pistons being mounted on the same rod. The gas compressed in the first cylinder enters into the second, acts in this as motive force, expands thereby, and is cooled at the same time. Of course the expansion must not be driven so far as to leave insufficient tension for employment in the carbonators, but the cooling is performed free of expense. [This reasoning and the invention based upon it are quite erroneous. The motive power gained in the second cylinder must be employed as an excess in the first cylinder, and the evolution or absorption of heat must go quite parallel to the mechanical work, so that in the end the gas will have the same degree of heat as it would have if directly compressed to the tension remaining in the second cylinder. The only gain will be the cooling by the surface of the second cylinder; but there will be more friction and more loss of power, so that there is no saving in the cost of cooling.]

For carbonating apparatus worked with low pressure the cheapest is no doubt a *fan-blast*; but this cannot be worked at a higher pressure than about 18 inches, unless two of them are combined in series.

Apart from the lime-kiln gas, *the carbonic acid formed on calcining the bicarbonate* is always utilized again in the manufacture. In theory this gas, after condensing the water, ought to be pure carbon dioxide; but it is actually far from this, and contains at most 50 per cent.  $\text{CO}_2$ . This is certainly much stronger than the best lime-kiln gas; many patents describe it as extremely useful for finishing the last stage of carbonation, and direct it to be introduced only occasionally in certain places. But, so far as I know, this is not actually carried out; these gases are simply mixed with the lime-kiln gases. Probably they are on the average not much richer in  $\text{CO}_2$  than lime-kiln gases, as much air is drawn into the calciners on pumping the gas away.

*The quantity of carbonic acid required and the dimensions of the pumps and engines* are calculated by Fassbender in Zsch. f. angew. Chem. 1893, p. 256, with the following final results:—A daily production of 10 metrical tons of soda-ash, taking account of losses in working, requires the equivalent of 11 tons of 100 per cent.  $\text{Na}_2\text{CO}_3$ . This is equivalent to 9132 kil.  $\text{CO}_2$  per day, or 380.5 kil.  $\text{CO}_2$  per hour; but as the expulsion of  $\text{CO}_2$  in the still is not quite perfect, we must assume 400.5 kil. The soda-calciner yields per hour 190.25 kil.  $\text{CO}_2$ ; but only half this is drawn out by the pump, and 10 per cent. is not absorbed in the carbonators, so that only 80.5 kil. is left as available, and the lime-kiln gas must furnish the difference:  $400.5 - 80.5 = 320$  kil.  $\text{CO}_2$ . Where working with 30 per cent. gas, the exit-gas from the carbonators normally contains 3 per cent., while 27 per cent. = 270 litres  $\text{CO}_2$  per cubic metre of gas is utilized. A litre of  $\text{CO}_2$  at  $25^\circ$  and 740 millim. pressure weighs 1.752 grams; 1 cubic metre lime-kiln gas therefore contains  $270 \times 1.752 = 473.04$  grams available  $\text{CO}_2$ , and 320 kil.  $\text{CO}_2$  corresponds to 676.5 cubic metres lime-kiln gas of  $25^\circ$  and 740 millim. pressure. This quantity must be increased by that required for raising liquids and for mechanical absorption, so that we arrive at 712 cub. metr. per hour or 197.8 litres per second. With an efficiency of 0.85 the piston in the compressor must work at the rate of 232.6 litres per second. Assuming 40 strokes per minute, this means a velocity of 1.2 metres ( $=47\frac{1}{2}$  inches) for the piston-rod, with a sectional piston-area of 0.194 sq. metre ( $=300.7$  square inches).

In order to calculate the dimensions of the steam-engine and the quantity of steam, we must take account of the resistance to

be overcome. This, in the case assumed by Fassbender, amounts to 1.83 atmospheres for the carbonating-tower, and 0.21 atmosphere for the three washers (for soda-ash, water, and acid); further 0.46 atmosphere for friction in the pipes, valves, &c.; total 2.5 atmospheres. With the before-assumed dimensions of the pump, this is equal to 45.8 indicated H.P. at the pump, or, putting the efficiency = 0.80, 56.6 indicated H.P. at the steam engine, when assuming the medium steam-tension at the inlet = 6 atmospheres and at the exhaust = 1.63, the latter being assumed on account of utilizing the steam in the ammonia-stills.

The above work can be performed by a steam-cylinder of 0.440 metre diameter (= 17.325 inches) and 0.900 metre stroke (= 11.81 inches), at 40 strokes per minute and a cut-off at one third of the stroke. The quantity of steam, inclusive of losses, at 27.2 kilog. (= 60 lbs.) per indicated H.P. per hour, is = 1538 kil. or 3384 lbs., of which 1096 kil., with a tension of 1.63 atmospheres, go to the ammonia-stills.

#### *Preparation of pure Carbonic Acid.*

According to the experience hitherto gained, the impure carbonic acid obtained as lime-kiln gas, especially after receiving the purer gas obtained on calcining the bicarbonate in suitable apparatus, is quite sufficient for the ammonia-soda manufacture. The increased expense for preparing entirely or nearly pure carbonic acid can hardly be expected to be warranted by its better action, and is practically so far nowhere incurred. We shall, however, make a short enumeration of the methods proposed for preparing such pure  $\text{CO}_2$ , apart from those destined in the first instance for converting the bicarbonate into soda-ash, which will be described in the 5th chapter.

#### *I. Preparation of pure Carbonic Acid by the action of superheated steam on calcium carbonate (or other earthy carbonates).*

Boulouvard (p. 29) at first prepared his  $\text{CO}_2$  by this well-known method, but soon abandoned it. Grouven (Germ. pat. 26248) and Leplay (Germ. pat. 28757, 29153) describe special forms of this method, especially for the use of sugar-works.

## II. *Various Processes.*

Parnell and Simpson (Engl. pat. No. 46, 1886) produce pure  $\text{CO}_2$  by heating ammonium bicarbonate (comp. 8th chapter).

Fawsitt (Journ. Soc. Chem. Ind. 1885, p. 92) proposes to use the carbonic acid from fermentation-processes for the ammonia-soda manufacture.

Knoop (French pat. 215329) proposes decomposing carbonates at a white heat by causing them to pass downwards in the annular space between two concentric cylinders.

Deacon (communication from Arnois, Engl. pat. 10759, 1887) passes water-gas through heated oxide of manganese or iron, whereby it is burnt to  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ; after condensing the former by cooling, pure  $\text{CO}_2$  remains behind. The metallic oxides are continually regenerated by passing hot air through them.

Compare also, in the 5th chapter, Staub's process for decomposing sodium bicarbonate by ammonia, with liberation of pure  $\text{CO}_2$  (Germ. pat. 45107).

Claus (Engl. pat. 15173, 1888) utilizes the same reaction, viz. expelling the  $\text{CO}_2$ , and retaining the  $\text{NH}_3$ , which escapes at a higher temperature, by condensing it with water; he thus produces pure  $\text{CO}_2$  by the application of ammonium carbonate. Schloesing and Rolland, many years before, had done much the same thing (p. 6); also Parnell and Simpson (comp. Chapter VIII.).

Margueritte (French pat. 57293, 1863) places equal quantities of ammonium carbonate in two apparatus; in one of these  $\text{NaCl}$  is dissolved, in the other sulphuric or hydrochloric is used for driving out the  $\text{CO}_2$ , and passing it into the first apparatus, in order to produce  $\text{NaHCO}_3$ . Hardly less costly than this proposal seems to be another, to obtain the  $\text{CO}_2$  by igniting a mixture of coal and copper oxide in a cast-iron retort, and to recover the spent oxide by calcining it in a current of air.

German patents for preparing  $\text{CO}_2$  by heating carbonates in the state of powder are those by Schütz (No. 79311) and Knoop (No. 79407).

## III. *Preparing pure Carbonic Acid by absorbing impure $\text{CO}_2$ in a solution of sodium carbonate, and decomposing the solution by boiling.*

The nature of this process is this:—On treating a solution of

sodium carbonate with gases containing  $\text{CO}_2$ , sodium bicarbonate is formed and the inert gases are removed. On boiling the solution pure  $\text{CO}_2$  escapes, and the remaining solution of  $\text{Na}_2\text{CO}_3$  need only be evolved to serve over again in the first stage. This process was proposed many years ago, *e. g.* in 1854, by Deacon (No. 1504), and in 1864 by Ozouf (No. 1498), and since then has been repeatedly suggested. Its technical possibility must be founded upon utilizing the heat of the boiled-out solution of sodium carbonate, as well as that of the  $\text{CO}_2$  and the steam escaping for heating up the solution of bicarbonate in the most rational manner.

Among the numerous later inventors who propose special forms of this reaction, I mention the following:—

Gossage (Engl. pat. 1442, 1872).

Fassbender (Germ. pat. 36702), who causes lime-kiln gas to meet the solution of  $\text{Na}_2\text{CO}_3$  in a column apparatus, and separates the  $\text{CO}_2$  from it by diminishing the pressure.

Luhmann (Engl. pat. 9171, 9646, 10158 of 1891; 6931 of 1892) describes an ingenious but complicated apparatus, as also do Behnke, Hell, and Sthamer (Germ. pat. 76130), and Hess (Germ. pat. 77377).

Rommenh  ller first takes a French patent for the old reaction of Ozouf, &c. (No. 213958), then another for employing sodium phosphate,  $\text{Na}_2\text{HPO}_4$ , as the absorbing agent; it is converted by  $\text{CO}_2$  into  $\text{NaH}_2\text{PO}_4$  and  $\text{NaHCO}_3$ , and this mixture is decomposed by heating into  $\text{CO}_2$  and recovered  $\text{Na}_2\text{HPO}_4$ .

## CHAPTER IV.

PRECIPITATION OF SODIUM BICARBONATE BY THE  
CARBONATING PROCESS.*The Solvay Tower.*

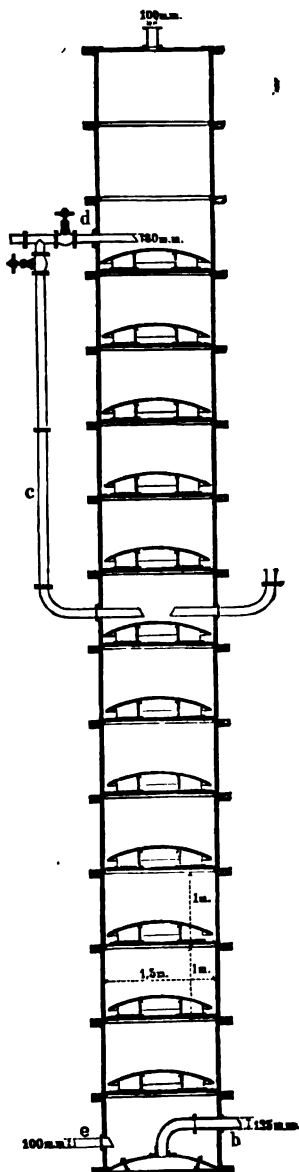
THE first apparatus constructed by Solvay, which worked too slowly, was by the patent of 1872 replaced by the well-known carbonating-tower, which is mostly identified with the Solvay process before everything else, and forms a salient outward feature of all works which have adopted his process. This apparatus, indeed, performs its function, although much modified in details, at all works connected with the Solvay syndicate, and probably also at some others (the patent having expired), whereas all other principal parts of the apparatus which have been the foundations of Solvay's reputation and pecuniary success seem to have been abandoned.

Fig. 20 shows the Solvay tower, figs. 21 & 22 one of the cylinders on a larger scale. The tower is built up from cast-iron cylinders or drums, formerly of a diameter of 5 feet, and 3 feet 3 inches high, as shown in the diagrams. Nowadays they are made of the same height, but 6 feet 8 inches wide. The bottom of each drum is formed by a cast-iron disc with a central opening 1 foot 4 inches wide. Over this is supported on light stays, *a a*, a sieve, shaped like a spherical segment, not quite reaching to the inner wall of the drum, and thus leaving a small annular channel all round, which permits the liquid and the gases to circulate even when the holes of the sieve are stopped up, and also allows the bicarbonate crystals to slide down on its curved surface and to drop on to the next plate. Formerly fifteen such drums were superposed over one another, as in the drawing, but now, as a rule, more of them, up to twenty-five, are employed.

The liquid enters at *c* under pressure, in the case of smaller towers about midway between top and bottom, in the larger ones about two-thirds up, and fills the tower to within 10 feet of the top; at *d* there is a branch for the upper, empty tower-space. The lime-kiln gas enters at the bottom at *b*, and is by the sieve-holes divided into very many bubbles, which unite again into a compact stream in the large central opening in the bottom of the next drum, where they are again divided by the sieve, and this is repeated over again in every compartment. In the same way the liquid descending in the tower is divided over and over again and brought into intimate contact with the gas-bubbles. At *e* the liquid, now filled with bicarbonate crystals, issues from the tower.

Solvay attaches great importance to the fact that the ammoniacal brine does not enter into the tower near the top, but a considerable way lower down. If it entered near the top, the gaseous current would carry away much free ammonia, which is more valuable than the ammonium carbonate; although, as we shall see, that ammonia would in no case escape unabsorbed into the outer air, yet its loss would impoverish the descending liquor. Since the entrance for the ammoniacal brine is placed further down, the layer of liquid above this point is still exposed to the action of the gases coming from below, which are certainly much poorer in  $\text{CO}_2$  than near the bottom, but are still able to

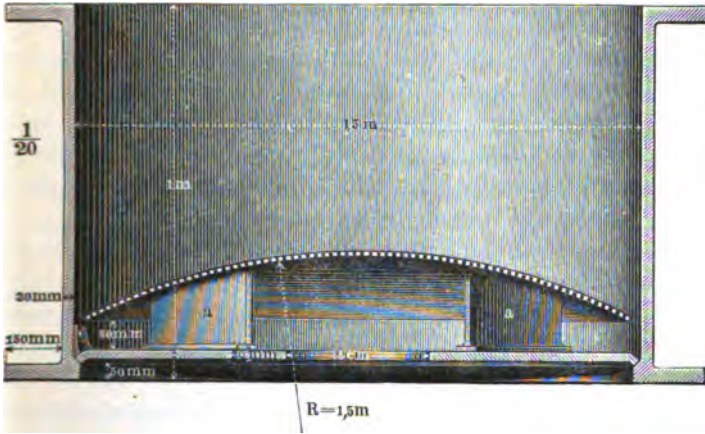
Fig. 20.



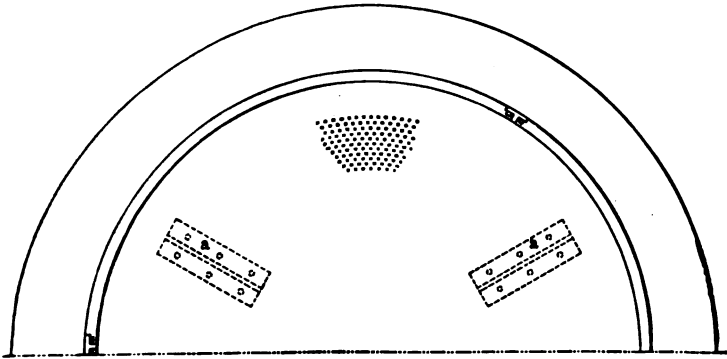


convert much free  $\text{NH}_3$  into normal ammonium carbonate, and thus to keep it back in the tower. [This task is certainly performed in a very ingenious way by the described construction, but it is more easily and safely effected by combining several absorbing apparatus in a set. As we shall see, it is not carried through in its original form at the Solvay works themselves.]

**Fig. 21.**



**Fig. 22.**



The ascending gas has, according to the height of the tower, to overcome a resistance of from  $1\frac{1}{2}$  to  $2\frac{1}{2}$  atmospheres, and must be furnished by the blowing-engine at a corresponding pressure. On

ascending, as the pressure diminishes, the gas must considerably expand, and the mechanical work of expansion absorbs considerable heat, which partly compensates the increase of heat arising within the tower by the chemical reaction, and prejudicial to the completion of the reaction. This is also put forward by Solvay as one of the principal advantages of his tower. Experience has, however, shown that the necessary cooling can be attained more cheaply and safely in other ways, and that, on the other hand, the lowering of the temperature, which is performed by the expansion of the gas in the Solvay tower, is nothing like sufficient.

Solvay also laid much stress on the fact that the gaseous stream must enter from below in sudden jets, and the liquid must equally issue at *c* in such jets, in order to prevent the settling down of the bicarbonate in special places, and thus obstructing the tower. This method has not been found to answer its purpose efficiently, and it seems to have been abandoned.

The utilization of the carbonic acid is stated by Pick (*Die Alkalien*, 2nd ed. p. 98) to be almost perfect, so that the exit-gas contains hardly anything but nitrogen, and only in the case of bad saturation or poor lime-kiln gas a little  $\text{CO}_2$  and sometimes  $\text{CO}$  are found. But such perfect utilization is probably very exceptional. Others, on the contrary, state that the exit-gases contain as much as 10 per cent.  $\text{CO}_2$  by volume, which is certainly too much according to present experience. At specially well managed works I was informed that the exit-gases tested from 3 to 4 volumes per cent. of  $\text{CO}_2$ , corresponding to a utilization of 80 or 90 per cent.

The liquid partly saturated with  $\text{CO}_2$  can dissolve more salt, and therefore some fresh salt must be put into the carbonators. This seems to have been done (and perhaps is still done) to a very considerable extent in the Solvay towers, whilst it has been abandoned at other works. At Solvay's they employ 15 or 20 parts of solid salt to 100 parts of salt contained in the brine. Solvay's patent, No. 1904 of 1876, prescribes mixing this solid salt with the strong brine introduced at the top of the tower for the purpose of retaining the ammonia.

Where great care is taken in the recovery of ammonia to cool and thereby to dry the gases, coming from the stills, as thoroughly as possible, it is possible to greatly reduce the quantity of salt to be added in carbonating, and it is asserted that at some places they do entirely without solid salt.

*Cooling of the Towers.*—The chemical combination of the carbonic acid with the other ingredients is a phenomenon connected with the evolution of much heat, and the rise of temperature effected thereby counteracts the formation of sodium bicarbonate by promoting a reversal of the reaction (p. 15). Hence from the outset both the ammoniacal brine and the lime-kiln gas is cooled down before use in the carbonator (pp. 34 & 48), but this must needs be supplemented by cooling during the carbonating process itself. This is promoted by the expansion of the gases within the Solvay tower, as shown on p. 56, but not to a sufficient extent. The towers were formerly cooled from without by large quantities of water flushed on to the top and running down the sides; but this also acts only imperfectly, considering the large diameter of the towers, especially those of greater width, as now used, and has been recently replaced by cooling from within, by means of the following apparatus.

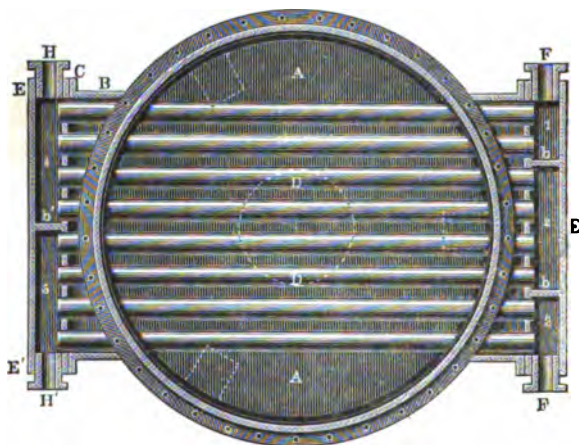
Cogswell (Engl. pat. 1973, 1887) applies a system of water-cooling within the tower, a stream of water passing through all the chambers one after another, and thoroughly refrigerating them in the very centre. This apparatus is now introduced at all works of the Solvay syndicate, and has made the flushing of the towers from without unnecessary. His apparatus is shown in figs. 23 & 24. The single cylinders A, A are provided with rectangular nozzles B, B at two opposite sides, closed by perforated flanges and similarly perforated plates C. The latter support the cooling-pipes D, D, which pass right through the cylinders and are tightly fixed in the plates C. The ends of the pipes D are contained in boxes, confined on the inner side by plates C, on the outside by covers E. These covers are provided with two partitions *b, b*, reaching up to plate C, and thus dividing the box into three compartments 1, 2, 3. In the two end compartments (1, 3) there are two, and in the middle compartment (2) four pipe-ends. The opposite box has only one partition *b'* in the centre, so that each of two compartments (4, 5) contains four pipe-ends. The cooling-water enters through F into compartment 1, flows through two pipes D into the opposite compartment A, then by the other two pipes D, ending in the same box, back into compartment 2, from here again into compartment 5, and from this at last into compartment 3; through C it overflows into the system of pipes belonging to the next cylinder. The couplings H in compart-

ments 4 & 5 serve for connecting the cooling sets belonging to two cylinders. The cooling is regulated in such manner that the upper portion of the tower is cold, but the lower portion remains warm enough for the liquid to run off at a temperature of  $30^{\circ}\text{C}.$ ; we shall see the reason of this further on.

Fig. 23.



Fig. 24.



Vivian and Bell (Engl. pat. 7527, 1890) propose cooling during carbonation by means of brine, in an apparatus very different from the Solvay towers, and to apply the heated brine for absorbing the ammonia, which seems contrary to all reason.

Much more heat is liberated in the first stage of absorbing carbonic acid by ammoniacal brine than later on. In the first stage normal ammonium carbonate  $(\text{NH}_4)_2\text{CO}_3$  is formed, and this produces much more heat than its conversion into bicarbonate.

Basing his process on that well-known fact, Solvay, in the patent No. 2173, 1876, further directed the introduction of  $\text{CO}_2$  in the upper part of the apparatus where brine is saturated with ammonia; the heat produced here by the formation of normal carbonate is removed in the tubular cooler (p. 34) before entering the carbonator. Later on, the Solvay works have developed this into putting up a second carbonator alongside the principal tower; in the former the ammoniacal brine is as much as possible converted into mono-carbonate, and is then transferred to the principal tower, where the precipitation takes place. They consequently always combine a large with a smaller tower: the cooled ammoniacal brine is first brought up to the state of  $(\text{NH}_4)_2\text{CO}_3$  in the smaller tower, and is then introduced into the other tower at three-quarters of its height; here more  $\text{CO}_2$ , preferably also that from the calciners, is introduced and the reaction of forming the bicarbonate is here completed. The magma formed here is continuously passed on to the vacuum-filters (see below) and washed there.

*Obstructions by Crusts.*—An important drawback of the Solvay towers is the inevitable gradual obstruction of the sieve-holes in the dividing-plates, which, in spite of the precautions mentioned above, takes place with such rapidity that each tower must be cut off on an average once a fortnight, in order to run off its contents and to remove the accumulated crusts by steaming or by hot water. As this heats the tower so much that it cannot perform its function, it must be cooled down by standing still or by cold water. In order not to interrupt the work, there must be a spare tower in reserve, so that, for instance, in a set of seven towers only six are at work, while the seventh is being steamed and then cooled. Usually this is done in the following manner:—The empty spare tower is connected with the tower to be cleaned out; half of the contents of the latter will then flow over into the former by its own pressure, and the other half is forced over by compressed air or lime-kiln gas. The tower to be cleaned, after all the liquor has been removed, is filled with water up to the level where crusts have been formed, and the water is brought to boiling heat by injection of steam. The escaping vapours contain both  $\text{CO}_2$  and  $\text{NH}_3$ , which must be retained by washing. If a sample of the liquid taken by means of a testing-tap shows complete absence of ammonia, the dissolution of the crusts will have sufficiently progressed. The liquor is now run off; it contains principally  $\text{NaCl}$

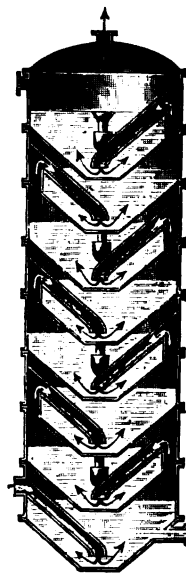
and  $\text{Na}_2\text{CO}_3$  in solution, but is mostly too dirty to be worked for soda-ash, and is best used up for purifying brine or dissolving salt.

The formation of crusts, both in the towers and in other apparatus, is principally caused by two circumstances, partially connected with each other, and both caused by irregularities in working. If the air-pump acts too slowly or altogether stops, the liquid will cease to be agitated, and the bicarbonate crystals will accumulate in certain places. In such cases the cooling will also be too strong, and this causes the bicarbonate to be separated in a fine muddy state, which not merely produces a difficulty in washing on the filters, but also more easily causes obstruction.

We have already remarked (p. 22) that magnesia promotes the formation of crusts.

Among other *forms of carbonating-towers or columns*, we only notice that invented by Schreib and constructed by Calow & Co. at Bielefeld (Germ. pat. 70169). It is shown in fig. 25, and consists of cylindrical parts with conical bottoms, not admitting of any accumulation of crystals on these bottoms. Moreover, the single compartments contain a comparatively large bulk of liquid, which diminishes the cooling and produces coarser bicarbonate. We must, however, ask whether the cooling is not diminished *too much*, and we refer to the general introduction of the Cogswell system of internal cooling, p. 57.

Fig. 25.



#### *Other Carbonators of upright Form.*

In Honigmann's process, as seen by me in 1878, the carbonating of the ammoniacal brine is not performed under very high pressure, but only at  $\frac{1}{4}$  to  $\frac{3}{4}$  atmosphere above ordinary pressure, with well-developed contact surfaces. He employs a set of three upright iron cylinders, 10 to 13 feet wide and of the same height, with conical bottoms, through which the lime-kiln gas is forced in succession, so that it has to pass through a total head of liquid of from 20 to 23 feet depth, in such manner that the gas is

equally divided over the total bottom area of each cylinder (about 90 superficial feet). The heating of the liquid is kept down by running water over the outside of the cylinders; the temperature is kept between  $25^{\circ}$  and  $35^{\circ}$  to produce a coarsely crystalline, easily filtering precipitate.

In a more recent patent (Germ. pat. 13782), Honigmann describes a precipitating column of very simple construction, 40 feet high.

Hugo Müller (of Düsseldorf) describes (Engl. pat. No. 4458, 1874) for the ammoniacal soda-manufacture an apparatus which can be used also in other cases where liquids have to be brought into intimate contact with gases. He employs several apparatus connected together, shaped like funnels at the bottom, and semi-circular at the top; a centrifugal pump moves the liquid from the lower into the higher compartment, pours it over a trough with perforated bottom and a filtering cloth above this, and thus divides it minutely, whilst the solid particles remain behind in the trough, which can be easily taken out.

Unger (German patent, No. 2295, Dingler's Journal, ccxxxi. p. 436) saturates the ammoniacal brine first with lime-kiln carbonic acid in an upright iron cylinder with a jacket for cooling-water, and a vertical quickly revolving shaft carrying disks, by which the liquid running down is violently splashed about. The fire-gases in the first apparatus travel downwards, in the second one upwards, so that the  $\text{NH}_3$  carried away can be washed out by  $\text{NaCl}$  solution. The solution of ammonium monocarbonate and common salt is now saturated in other cylinders with pure  $\text{CO}_2$  from decomposing the  $\text{NaHCO}_3$  under pressure. For more easily absorbing the  $\text{CO}_2$ , narrow spirals are fixed in the cylinders, which distribute the  $\text{CO}_2$ , and by their mobility prevent the adhesion of crusts to them. The saturation of brine with  $\text{NH}_3$  takes place in a cylinder fitted with small upright tubes, each tube being a little to one side of the pipes below. In similar apparatus the last remnant of  $\text{NH}_3$  is washed out of the escaping pure  $\text{CO}_2$  and the fire-gases.

Schreib (Chem. Zeit. 1890, p. 492) also recommends a set of three cylinders with conical bottoms, into which the gas is forced at the lowest part, so that the precipitate, which cannot attach itself to the slanting sides of the lower part, is well churned up. The division of the gas is promoted by several perforated partitions.

The three cylinders are connected with each other in such a way

that every one of them can serve as first, second, or last of the series.

The American patents of H. Frasch (Nos. 361335 361622, 418315) contain a number of special proposals for the ammoniacal soda-manufacture.

### *Horizontal Carbonators.*

These form another type of apparatus for treating the ammoniacal brine with carbonic acid. One of the oldest of its kind, founded on very commendable constructive principles, is that of Gossage (Engl. pat. No. 422, 1854). It is shown in figs. 26 & 27, and consists of a cylindrical vessel, divided into six chambers,  $a_1$  to  $a_6$ , by partitions which do not quite join; it rests on the spindles  $a$  and  $b$ .  $a$  is solid, and is slowly turned round by the gearing  $e$  and  $f$  connecting it with the main shaft  $g$ ;  $b$  is hollow, and runs into two glands, which leave between them a chamber into which two gas-pipes for  $\text{CO}_2$  and  $\text{NH}_3$  enter, which communicate with the hollow spindle by openings, allowing the gas to pass through;  $d$   $d$  are openings closed by lids for introducing the

Fig. 26.

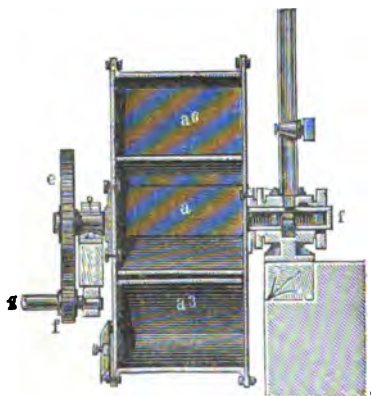


Fig. 27.



materials. The solution is run in above the axis; on the cylinder turning round it is scooped up by each chamber in turn, and is poured out again as each reaches the position of  $a_1$ . At the same time the gas rises through the liquid in bubbles; so that it is well mixed with and absorbed by the latter. At first the gases are



introduced without pressure; at last the  $\text{CO}_2$ , in order to produce complete saturation, must be forced in with an excess pressure of at least 10 lb. to the square inch. Since in the condensation of gas much heat is given off, the solution must be cooled down at least to  $37^\circ \text{C}$ . before running it out. In the cylinder a solution of 1 part of salt in 3 parts of water is employed; the  $\text{CO}_2$  is partly obtained by heating the sodium bicarbonate formed in the process in iron retorts. In place of the mixing vessels described, a coke-tower can be employed, in which the gases ascend and the solution runs down. To the saturated solution of salt either so much solid ammonium sesqui- or bicarbonate is added that 17 parts of  $\text{NH}_3$  are present for each 240 parts of brine, or into 240 parts of brine the  $\text{NH}_3$  gas given off from 54 parts of  $\text{NH}_4\text{Cl}$ , and afterwards  $\text{CO}_2$  under a pressure of 10 lbs. per square inch, are passed. After the decomposition is finished, the mixture is filtered through canvas in a closed vessel; here the mass is first drained and the  $\text{NH}_4\text{Cl}$  mixed with the  $\text{NaHCO}_3$  then displaced by a solution of pure  $\text{NaHCO}_3$ .

Schloesing's apparatus of 1858 (p. 5) also consisted of horizontal cylinders, provided with quickly turning agitating-blades which cause the liquid to squirt about; they are mounted terrace-way, and work continuously, the liquid entering the top cylinder and leaving the bottom cylinder as a magma of bicarbonate crystals and solution of ammonium chloride, the carbonic acid travelling the opposite way.

The apparatus patented by J. Young (No. 2558, 1871) combines the preparation of ammoniacal brine with the carbonating of the same. It is shown in figs. 28 to 30: fig. 28 is a front elevation; fig. 29, a plan; fig. 30, a back elevation. It consists of three cylindrical, air-tight, iron vessels, A, B, and C, carried by journals D, revolving in bearings E fixed in the framing F. Beneath each of the cylinders a fire-grate, G, is situated; and at one end of each vessel a bevel wheel, H, is attached. The wheels H are in gear with bevel pinions, I, carried on short vertical shafts, J, each of which has at its lower end another bevel pinion, K, in gear with similar bevel pinions, L, on the horizontal shaft M. The pinions L are provided with levers, N, movable on studs, O, by which the pinions L can be thrown in and out of gear with the pinions K when required. Any two of the cylinders A, B, C communicate by pipes passing through the hollow journals D of any other of

the vessels. We will assume that the vessels A and B are in communication by the pipes *a* and *b* provided with stop-cocks *c*, *d*, *e*, and *f*.

Fig. 28.

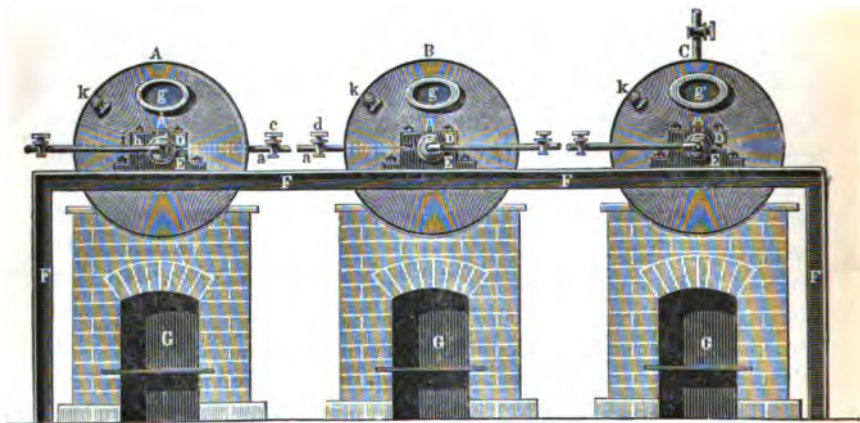
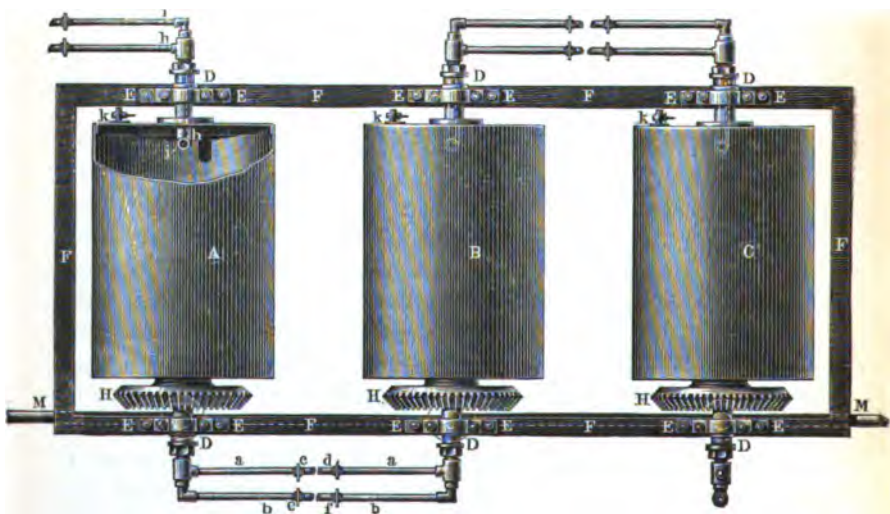


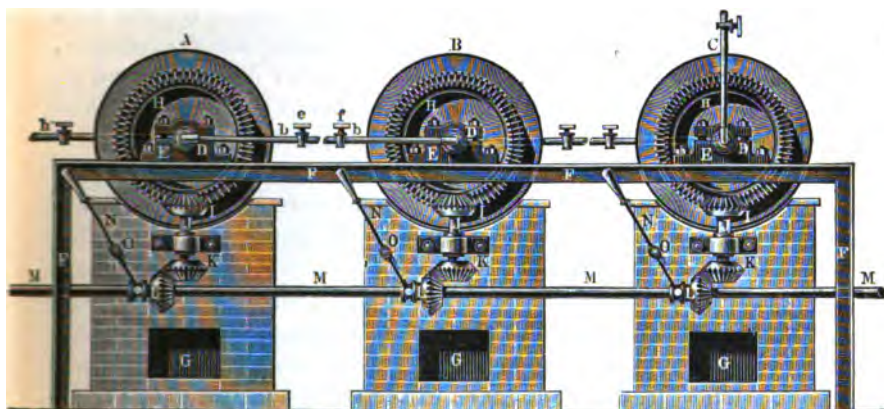
Fig. 29.



In commencing the operation the door *g* in the end of the vessel A is removed and a solution of salt (1 part in 3 parts of water) run

in ; its surface must be well below the ends of the pipes *h* and *i*, which may be turned upward inside the vessel, as shown in fig. 29.

Fig. 30.



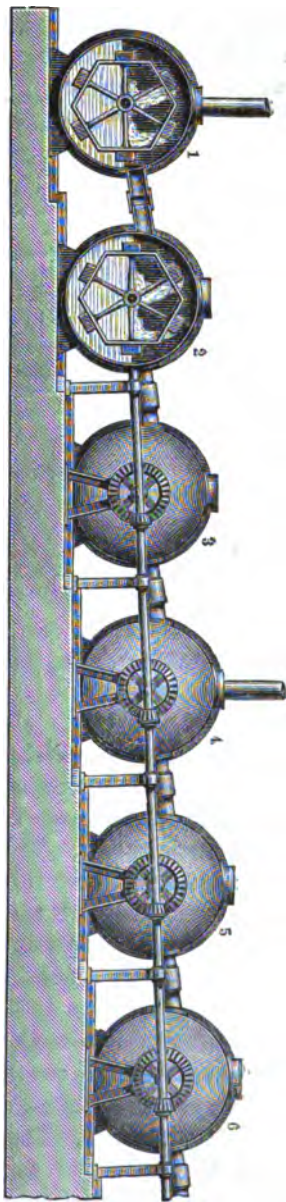
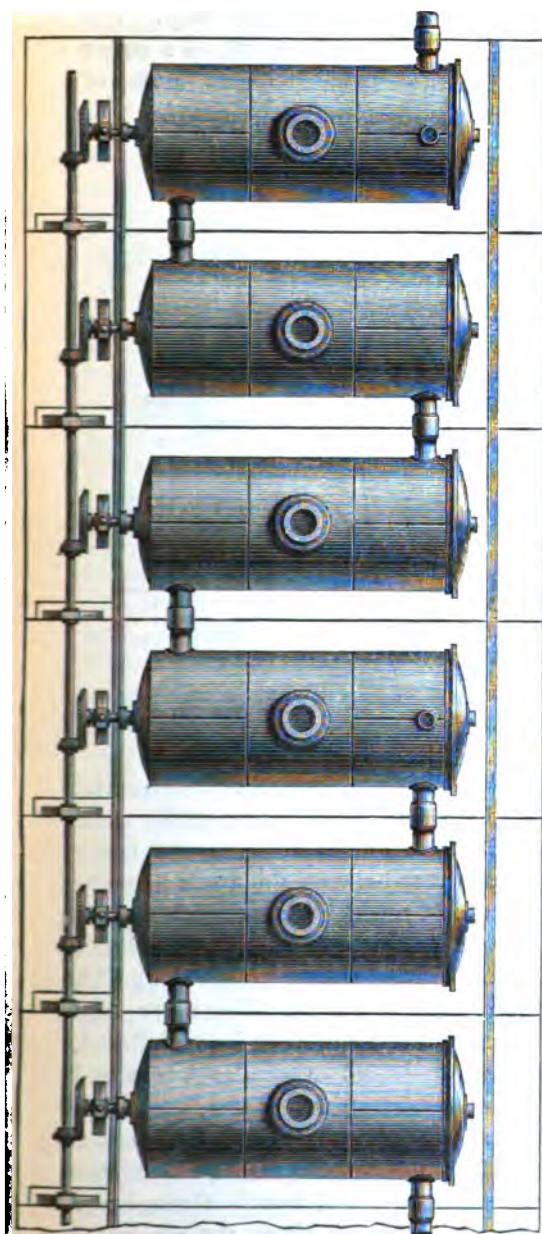
The door *g* is closed air-tight; through *h* ammonia gas, in the proportion of 35  $\text{NH}_3$  to 100  $\text{NaCl}$ , is admitted; through the pipe *i*, passing through and ending above the pipe *h*, carbonic acid is introduced, obtained by heating sodium bicarbonate or from calcium carbonate heated to redness in a retort with steam passed through it. By causing the vessel A to revolve, fresh surfaces are constantly exposed; this may be assisted by perforated disks or a series of arms inside the vessel. When sodium bicarbonate begins to be precipitated, the temperature is kept at  $50^\circ \text{C}$ . The admission of  $\text{CO}_2$  is continued until absorption ceases. During this time the unabsorbed gas passes over through the pipes *a*, *b* into the vessel B, in order to act upon a fresh charge of salt water and ammonia. In B less than 3 water to 1 salt is contained, viz., by as much as passes over from the ammonia-still and in the subsequent heating of the bicarbonate solution in A. After the absorption is complete, the rotation of A is stopped, the bicarbonate allowed to settle, the solution of ammonium chloride discharged into the ammonia-still through the cock *k* and a pipe which is temporarily affixed; the remaining salt may be washed with water or a solution of common salt, and the washings also run into the still. Water is then added to the bicarbonate, and the vessel A gradually heated to the boiling-point,  $105^\circ \text{C}$ . The boiling may be effected by superheated

steam instead of an open fire. Thus any ammonia still present and half the carbonic acid are expelled; they first pass through a refrigerator, and then into the vessel B; the solution remaining in A is worked either for crystal soda or soda-ash.

The principle applied here, viz., saturating with  $\text{NH}_3$  and  $\text{CO}_2$  at the same time, has been rejected by most other inventors, probably with good reason. Young's apparatus does not seem to have been practically used, and at all events was not an economical success; but its mechanical principles seem to be quite sound.

Boulouvard's carbonating apparatus (French pat. 125625, of 1878) has been successfully employed at several French works. It is represented in figs. 31 and 32, and consists of a number of horizontal cylinders mounted one above the other. The ammoniacal brine enters the top cylinder and gradually passes downwards to the bottom cylinder, from which it issues, the carbonic-acid gas travelling the opposite way, as in Schloesing's apparatus, p. 6. The three bottom cylinders receive the pure gas from calcining the bicarbonate; the lime-kiln gas enters the fourth cylinder from the bottom. In Schloesing's apparatus the contact between gas and liquid was brought about by violent agitation, which requires much power and raises the temperature. Boulouvard employs instead of this a slowly turning bucket-wheel. The buckets, fixed on the periphery of the wheel, lift the liquor and pour it out again at the top into the gaseous atmosphere; on descending they force a certain quantity of the gas below the level of the liquid. This requires but little motive power, the bicarbonate is always borne along, and is carried downwards with the liquid through the wide connecting-tubes between the cylinders. If the wheels have to be stopped for some reason, the bicarbonate settles down as a heavy dense mass, which offers great resistance on again starting the machinery; the apparatus must therefore be substantially constructed. Ten cylinders, requiring one H.P. each, suffice for producing 10 tons of soda-ash in 24 hours.

Péchiney in 1880 (Engl. pat. Nos. 2098 & 5394) patented a modification of Boulouvard's apparatus which has actually been used at his works, and is shown in figs. 33 to 36. A is a large horizontal cylinder, turning round its axle. A horizontal perforated partition *b* runs along its entire length; there is also a number of vertical partitions *a, a*, with central holes *o, o* and manholes *z, z*. Ammoniacal brine enters through a hollow



Figs. 81 and 82.

trunnion C, and the waste gas escapes in the same way. The inner tube *g* of the other trunnion B (shown in fig. 35 on a larger scale) is divided lengthwise into two compartments, each of which communicates by *i* with the descending branch *j*. This

Fig. 33.

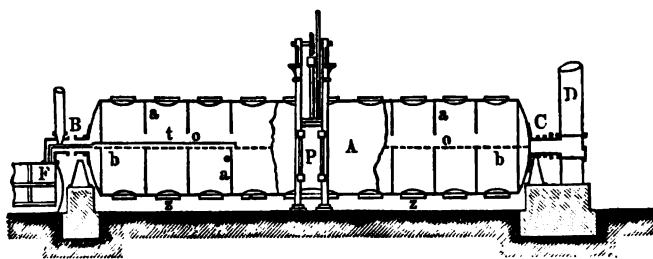


Fig. 34.

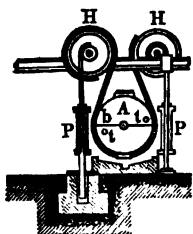


Fig. 35.

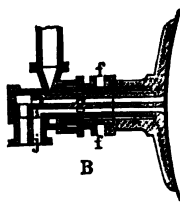
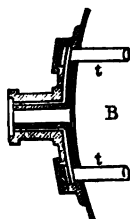


Fig. 36.



tube *g* serves for discharging the magma of liquor and bicarbonate, and for introducing strong  $\text{CO}_2$  from the calciners, while weak  $\text{CO}_2$ , in the shape of lime-kiln gas, enters through the outer concentric tube *f*. The annular space between *f* and *g* is laterally connected with two tubes *t, t* (fig. 36), which pass along the main partition *o* through the first three compartments, so that the lime-kiln gas enters only into the fourth compartment, the strong  $\text{CO}_2$  having already passed through *g* into the first. The inner tube bends down into a trough F, where the bicarbonate is precipitated, and where the pure  $\text{CO}_2$  is first introduced. Cylinder A is moved by means of the two hydraulic accumulators P P and the pulleys H H, so as to make first half a turn to one side and then half a turn to the other. The ammoniacal brine enters through D and the axle C into the last compartment of A, and travels through *o, o* from one compartment to the other, taking along the suspended bicarbonate with the assistance of the buckets, till it arrives in the



trough F. The  $\text{CO}_2$  travels in the opposite direction, so that the liquid meets with constantly stronger gas and at last with pure  $\text{CO}_2$ .

Other carbonating apparatus have been patented by Montblanc and Gaulard (Engl. pat. 4737, 1878, and Germ. pat. 14193); the Société anonyme des produits chimiques du Sud-Ouest (Germ. pat. 18709); Wigg (Engl. pat. 8125, 1882; 4436, 1885; 9227, 1887); Strassburger and Frauenkron (Germ. pat. 24982); Soc. an. des prod. chim. de l'Est (Germ. pat. 28761); Pick (Engl. pat. 7831, 1885; 4388, 1886); Soc. an. pour l'étude de soudières (Engl. pat. 9366, 1886); Burns (Engl. pat. 15352, 1886); Howitt (Engl. pat. 3657, 1891).

Excepting Solvay, most inventors have preferred combinations of several smaller carbonators, upright or horizontal, to the large towers working singly. Undoubtedly the Solvay towers fulfil their purpose in a most satisfactory way; and as they are used at all the works of the Solvay Syndicate, by far the greatest quantity of ammonia-soda is made in them. Indeed the great technical and economical success achieved by Solvay dates from the time when he invented these towers (1872). But I cannot help looking upon this more as a coincidence than a cause. The continuity of work, which is claimed as one of the advantages of the Solvay towers, is quite as well attained by the older and more recent combinations of several small carbonators in a set, in which the utilization of the carbonic acid can be effected at least as well as in the towers, while the control of the work is easier and no lofty buildings are required. The most important consideration is this: that the pumping of the gas requires much less motive power and the removal of the crusts is much easier than in the Solvay towers.

The intimate contact between the carbonic-acid gas and the liquid is accomplished by different means. Some, as we have seen, employ perforated partitions, others mechanical agitation. The former seems most simple, but does not act so well as the latter, and needs more power, since the gas has to be forced through a corresponding depth of liquid; in the case of mechanical agitators, which cause the liquid to be squirted about, the gas can be introduced above the level of the liquid under very small pressure, so that the force expended, inclusive of that required for driving the agitating-gear, is much less than for the large blowing-engines used in the first-mentioned system.

*The continuous style of working* is most easily conducted with sets of horizontal cylinders, or else with one such cylinder very long, as in the P  chiney-Boulouvard apparatus (p. 66). If several cylinders work together, they must be connected by very wide channels, to prevent being obstructed by bicarbonate. This capability of obviating obstructions and crusts forms one of the advantages of mechanical apparatus in comparison with Solvay towers. Of course the  $\text{CO}_2$  gas is always made to travel the opposite way to the liquor; if any separation at all is made, the richer gas from the bicarbonate calciners is introduced in the cylinder where the reaction is finished, and from which the magma is taken away to the filters; later on the lime-kiln gas is mixed with it, and every one of the cylinders is cooled by external flushing to the degree best suited for that stage of the process. The ammoniacal brine enters at the opposite end and meets the gas after this has lost most of its  $\text{CO}_2$ . As the gas escaping from here, and consisting mainly of nitrogen, must carry away much ammonia vapour, it is, of course, as mentioned in connexion with al hitherto described apparatus, passed through fresh brine in order to retain the  $\text{NH}_3$ . This can be done either in a column or by means of a mechanical agitator. To finish with, it is safest to employ a small coke-scrubber fed with sulphuric acid before the gas is ultimately sent into the air, although we must state that with proper work nothing should be left to be absorbed by the acid.

Fassbender (Zsch. f. angew. Ch. 1893, pp. 139 & 165) follows up the course of the ammonia in the Solvay apparatus in the following manner:—

The brine is made up to 70 grams ammonia per litre in the saturators\*. This liquor is introduced in the second compartment of the tower from the top; the top compartment receives about one-sixth of the volume of ammoniacal brine in the shape of purified fresh brine, to wash the gases before leaving the tower. The mixture of these two liquors is effected only in the third compartment, and the process is continued as if we had commenced with brine titrating 6 per cent.  $\text{NH}_3$ , but in such manner that the exit-gases carry away but little  $\text{NH}_3$ . We therefore assume as starting point for the following considerations a brine containing 60 grams  $\text{NH}_3$ , 270 grams  $\text{NaCl}$ , a little  $\text{CO}_2$ ,

\* This is more than is usually attained at the works, comp. p. 32, and is only accomplished with great extra care. The ordinary average is probably nearer 65 grams  $\text{NH}_3$ .



and about 0.5 gram  $\text{NH}_3$  in the shape of sulphate (caused by the gypsum contained in the rock-salt).

After blowing this liquor out of the tower we find the  $\text{NH}_3$  distributed as follows:—

1. About 0.9 per cent.  $\text{NH}_3$  in the mother liquor as carbonate.
2. About 4.6 per cent.  $\text{NH}_3$  in the same as chloride.
3. About 0.5 per cent.  $\text{NH}_3$  in the exit-gas from the tower.

Item No. 1 goes into the ammonia-still; the small quantity of this adhering to the moist bicarbonate can be neglected. Item No. 2 mostly goes into the ammonia-still; a certain portion adheres to the moist bicarbonate as well as some  $\text{NaCl}$ , and causes the finished ash to test only 97 or 98 per cent.  $\text{Na}_2\text{CO}_3$ . This corresponds to 0.08 per cent.  $\text{NH}_3$ , which is found in the gases drawn out from the calciner and is absorbed by brine. Item No. 3 is carried by the exit-gases into a brine-washer, where 0.3 per cent.  $\text{NH}_3$  is retained and at once utilized in the ammonia-saturator; the other 0.2 per cent. goes into a second washer, where 0.17 per cent. is retained by water serving for dissolving salt and afterwards for purifying the brine from gypsum, and the remaining 0.03 per cent. is retained by the acid-scrubber.

In order to calculate the quantity of liquor required for a daily production of 10 tons soda-ash, Fassbender makes the following assumptions:—manufacturing loss=10 per cent. of the finished product; increase of volume of the brine by passing in 7 per cent.  $\text{NH}_3$ =9 per cent.; on mixing ammoniacal brine with fresh brine-ash, no contraction; the gases from the ammonia-stills carry over 4 tons \* of distillate; the moist bicarbonate carries along 5 tons of water; the filtration requires 9 tons of washing-water; the fresh purified brine contains per litre 307 grams  $\text{NaCl}$ , 890  $\text{H}_2\text{O}$ , 2.3  $\text{NH}_3$  as carbonate and 0.57 as sulphate. After being diluted by the washings, the mother liquor contains 850 c.c.  $\text{H}_2\text{O}$  per litre.

To manufacture 10 tons of soda-ash for sale, we must prepare 11 tons as bicarbonate, and we must convert

$$\frac{11,000}{57} \times 17 = 3528.3 \text{ kil. } \text{NH}_3 \text{ into } \text{NH}_4\text{Cl.}$$

As in 1 litre of brine, containing 6 per cent.  $\text{NH}_3$ , 4.6 per cent. are converted into  $\text{NH}_4\text{Cl}$ , the above 3528.3 kil. correspond to

$$\frac{3528.3}{46} = 76.7 \text{ cub. metres brine of 6 per cent. } \text{NH}_3 = 4602 \text{ kil.}$$

\* By "tons" we understand here metrical tons of 1000 kilograms.

alkalimetrically proved  $\text{NH}_3$ . This 6-per-cent. brine is obtained by mixing the 7-per-cent. brine with 11·3 cub. metres of fresh brine, containing already 2·3 grams  $\text{NH}_3$  per litre as carbonate, or 26 kil.  $\text{NH}_3$ ; deducting this from the above 4602, we find 4576 kil.  $\text{NH}_3$ . This corresponds to  $\frac{4576}{70} = 65\cdot4$  cub. metr. 7-per-cent. brine + 11·3 fresh brine, or in all 76·7 cub. metr. 6-per-cent. brine.

The 65·4 cub. metres 7-per-cent. brine are composed of:—

56·3 cub. metr. fresh brine, containing  $56\cdot3 \times 307 =$

17284·1 kil. salt.

5·1 increase of volume (9 per cent.).

4·0 water, &c., carried over from the ammonia-still.

---

65·4 cub. metr. at  $\frac{17284\cdot1}{65\cdot4} = 264\cdot2$  kil. salt.

+ 11·3     „     fresh brine =  $307 \times 11\cdot3$  kil. salt = 3469·1     „

---

76·7     „     6-per-cent. brine with total salt = 20753·2     „

Hence 1 cub. metr. 6-per-cent. brine =  $\frac{20753\cdot2}{76\cdot6} = 270\cdot6$  kil. salt.

For 10 tons soda-ash we require 20753·2 kil. pure  $\text{NaCl} = 21$  tons rock-salt. [This quantity may be diminished by longer carbonating and more ammonia, but at the expense of increasing the other materials.]

The daily consumption of brine amounts to:—

For the 7-per-cent. brine from the  $\text{NH}_3$  absorbers,     56·3 cub. metr.

For the brine-washers in the carbonat.-towers     11·3     „

---

67·6     „

Containing  $67\cdot7 \times 890$  water ..... = 60164 litres.

Add to this condensing-water ..... 4000     „

„ washings from the filters ..... 9000     „

---

73164     „

Deduct water in moist bicarbonate ..... 5000     „

---

Left as contained in mother liquor ..... 68164     „

As the mother liquor contains 850 litres per cub. metre, the above is  $= \frac{68164}{850} = 80.2$  cubic metres, containing the following quantities of ammonia :—

NH <sub>3</sub> as sulphate	(0.05 + 0.03) × 76.7 × 10...	61.36 kil.
„ bicarbonate	0.9 × 76.7 × 10 .....	690.30 „
„ chloride	4.52 × 76.7 × 10 .....	3466.84 „
		<hr/> 4218.50 „

The *daily testings* at the carbonators are made as described in the case of ammoniacal brine, p. 32. In the present case the quantity of “free” NH<sub>3</sub> (that which passes away on boiling) is of course much less than the “fixed” NH<sub>3</sub> (present as chloride or sulphate). Sometimes the testing only extends to titrating the quantity of “free” NH<sub>3</sub> by standard acid and methyl-orange.

The *carbonic-acid treatment* is never carried on to complete saturation, as the last portions of CO<sub>2</sub> would be very slowly absorbed. Complete carbonation produces a more complete conversion, and therefore saves some NaCl, but it requires too much time, space, capital for plant, and cost of pumping CO<sub>2</sub>. According to Schreib (Chem. Zeit. 1890, p. 492), it is best to stop when the “free” NH<sub>3</sub> (estimated by titrating the filtrate with standard acid) is = 17 grams NH<sub>3</sub> per litre. It is possible to go down to 3 grams NH<sub>3</sub>, but with the above-mentioned diminution of the work done by the plant.

Schüchtermann and Kocke (Germ. pat. 21590) propose completing the reaction, when no more bicarbonate is separated, by adding to the filtrate caustic soda or ammonia and again carbonating. [This will hardly pay !]

The *degree of utilization of the carbonic acid* in the case of Solvay towers has been already discussed, p. 56. Other inventors generally assert that with their apparatus the CO<sub>2</sub> is much better utilized, but I cannot judge how far this is correct. Jurisch (Chem. Ind. 1890, p. 46) points out an error frequently committed in calculating the degree of utilization of a gas, and gives a formula of his own for this purpose.

Verzijl in 1875 (Nov. 19) obtained a French patent for employing carbonic acid compressed to three atmospheres, which is supposed to promote the conversion of ammoniacal brine into bicarbonate, as much more CO<sub>2</sub> is dissolved under high pressure.

He employs several apparatus in succession, in which the  $\text{CO}_2$  is systematically utilized. According to a letter I have received from the inventor, dated Oct. 23rd, 1881, the process had been tried on a small scale, but successfully. The gas on entering contained 22 to 25 per cent.  $\text{CO}_2$ , on leaving at most 1 per cent., and it carried away no more than 25 parts  $\text{NH}_3$  out of 2000 employed. I have heard nothing further of this process.

I have in several places referred to the *temperature* to be maintained in the carbonating process (pp. 12, 56, 57, 60, 70). I will therefore here only remark, generally, that in any carbonating apparatus, during the principal reaction, the temperature should not be below  $30^\circ \text{C}$ . (some say  $40^\circ$ ), since at a lower temperature the sodium bicarbonate does not separate in a coarsely crystalline form, but as a badly filtering mud. Later on, when the principal reaction has taken place, the temperature may be lowered to precipitate more bicarbonate. This is more easily done in the apparatus consisting of several combined vessels than in the Solvay towers as they were before the introduction of the Cogswell system of internal cooling. Under no circumstances must the cooling be carried to the point where ammonium chloride crystallizes out, which takes place at  $10^\circ \text{C}$ .

*Washing of the Exit-gases from the Carbonators.*—These gases, consisting mainly of nitrogen, with a small quantity of carbonic acid, must, of course, not escape freely into the atmosphere, but must be deprived by washing of the ammonia they carry away, just like all exit-gases of the ammonia-soda manufacture (comp. *e. g.* p. 33). This is done by means of a small coke-tower or by columns fed with fresh brine; the small quantity of  $\text{NH}_3$  thus absorbed may be increased by always employing two washers alternately, and feeding one with brine which has already served in the other. Sometimes another washer, fed with pure water, follows upon the brine-washers. The final washing is best made by a small coke-scrubber fed with dilute sulphuric acid, to absorb the last traces of ammonia (*e. g.* by Fassbender, p. 71); but if the previous washing has been thoroughly performed, there is hardly anything left for the acid-washer.

## CHAPTER V.

### FILTERING, DRYING, AND CALCINING THE BICARBONATE.

#### I. *Filtration.*

ACCORDING to Solvay's patents, every half-hour a certain portion of the contents of the absorbing-towers is drawn off, and the pasty mixture separated into a solution of ammonium chloride with a little carbonate and sodium chloride on the one hand, and solid sodium bicarbonate on the other. For this purpose he prefers vacuum-filters, consisting of iron cylinders of about 10 feet diameter and 5 feet high, in which the filtering-material lies upon a grating. It consists of a linen or woollen fabric, covered by a wire gauze or a finely perforated metal plate. Below this strainer a vacuum is made by an air-pump, and the mother liquor sucked off very quickly; water is now squirted by a rose very uniformly over the fine-grained bicarbonate; and this is continued till the salt smells little or not at all of ammonia. According to the patent No. 1904, of 1876, the water is to be applied warm, in order more effectually to dissolve any sal-ammoniac crystals. It is not possible, however, to remove all the ammonia by washing the salt without dissolving much bicarbonate; and this is a source of loss of ammonia. Or else the liquid may be heated, after being run out of the tower, in order to dissolve any sal-ammoniac crystallized out. Such a vacuum-filter is shown in fig. 37.

Fig. 38 shows the way in which the vacuum-filter is connected with the carbonating-tower. It consists of the cylinder T and the perforated false bottom *d*, supporting the filtering-medium. The magma of crystals and liquor arrives through K from the tower, and is by the turning cross Z equally divided over the filtering-medium. When enough of it has been introduced, the tap *x* is closed, and through *y* water is run in for washing. The vacuum is produced by the vessel Q, into which the liquid enters through the pipe W (comp. Engl. pat. No. 999, 1876).

The vacuum-filters are made of *cast-iron*, partly because these support the pressure from without better than wrought-iron

Fig. 37.

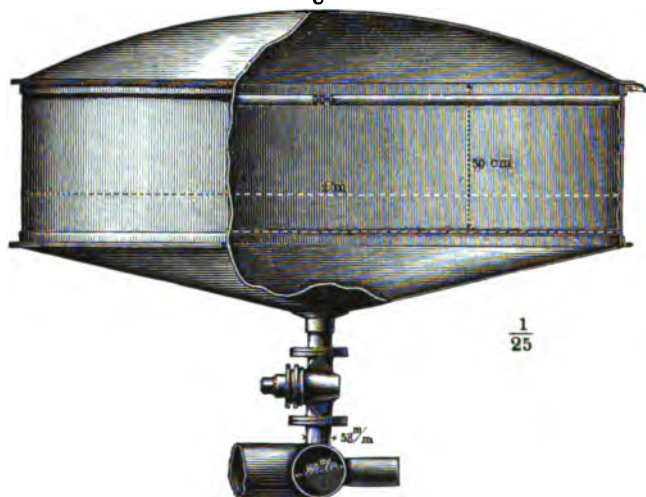
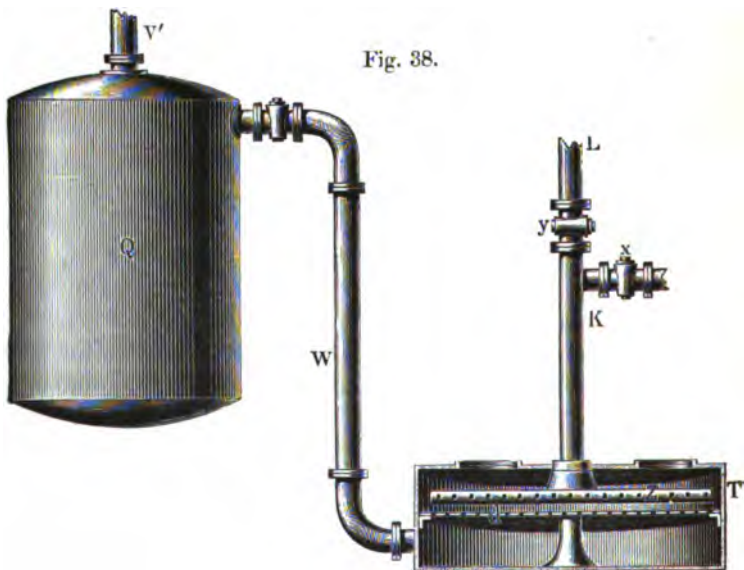


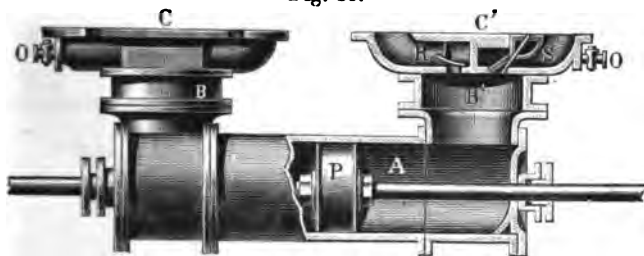
Fig. 38.



vessels, and partly because cast-iron better resists the attack of the ammonium chloride solution. So long as the liquor is alkaline, it can hardly act upon the iron, but after the alkali has been washed out, wrought-iron is quickly acted upon, especially in the presence of air. The grating which supports the filtering-cloth is also composed of strong cast-iron segments, supported on bearers at the circumference and in the centre.

The vacuum is produced, according to Solvay, by a pump with a "water-piston," fig. 39. Such pumps have no dead spaces, and they have in the present case the advantage of washing the gases

Fig. 39.



before ejecting them into the atmosphere. The piston P moves in the barrel A; B and B' are the water-pistons, C and C' the covers, B pressure-valve, S aspirating-valve, O a small tap for introducing liquid into the cylinders. This pump evacuates the vessel Q (fig. 38) through pipe V', and thereby draws away the liquid from underneath the false bottom *d* by pipe W. From Q the liquor goes into the ammonia-stills. Two or more such vessels, placed underneath the filter, are used in rotation. The air-pump may also serve for raising the liquid. The precipitate may be dried on the filter itself, by passing a current of dry air through it.

A very ingenious, but somewhat complicated, filter is that described in Solvay's patent, No. 1904, 1876, and shown in figs. 40 to 43. It consists of a cylinder with a paraboloid bottom A, divided by partitions into eight compartments, which are converted into as many filters by covers A<sup>1</sup> to A<sup>8</sup>. The bottom of A is continued in the centre into a cylinder D D, divided into the same number of compartments, and forming continuations of the filters A<sup>1</sup> to A<sup>8</sup>. These are provided with openings at the bottom, C, C, communicating with a box B, divided into three compartments (fig. 43). In this box a vacuum is continuously produced by an air-pump. By turning it the openings are put into communication with any one of the openings C, C, and thus, as in a Clegg's gas-distributor, the gas and liquor are directed in any given way, so that the liquid passing through the filter can be brought into any one of the vessels R to R<sup>iv</sup>. At first the space above the filters is charged with magma, and the filtering-liquid is run into a separate reservoir. After one of the eight sectors has been filled with crystals, the apparatus is made to perform an eighth of a revolution, whereupon the same sector receives washing-

Fig. 40.

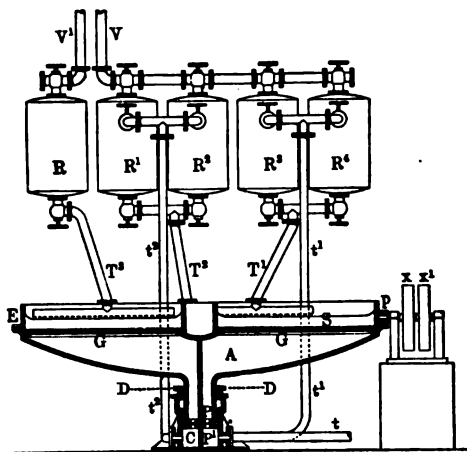


Fig. 41.

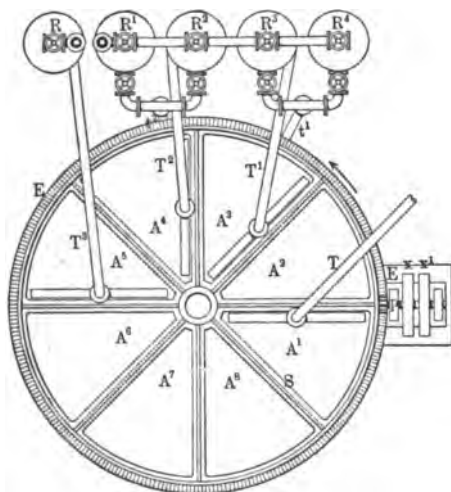
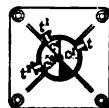


Fig. 42.



liquor which has repeatedly served before, and the liquid now running off, the distributor having changed its position, is carried to another reservoir. Thus the work continues, applying constantly purer washing-liquids, and at last a solution of pure sodium carbonate or bicarbonate; the washed-out salt is ultimately removed from the sector by mechanical means. I have not myself seen this apparatus in operation; but I am told that it works well at Varangéville.



Boulouvard's filtering-apparatus (French patent 114851, 1876) is shown in figs. 43 and 44 on a scale of 1:20. It is constructed with much skill, and has proved very successful at several French works. Its principal part is an hydraulic press, whose basement

Fig. 43.

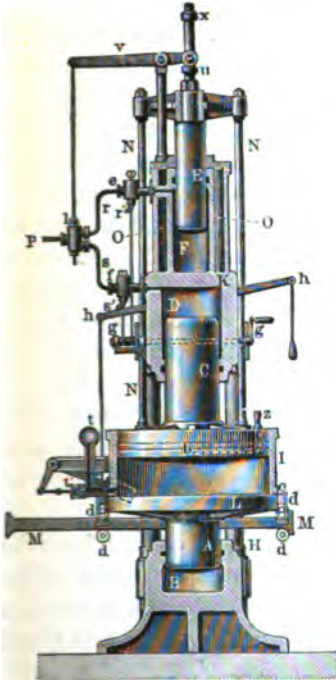
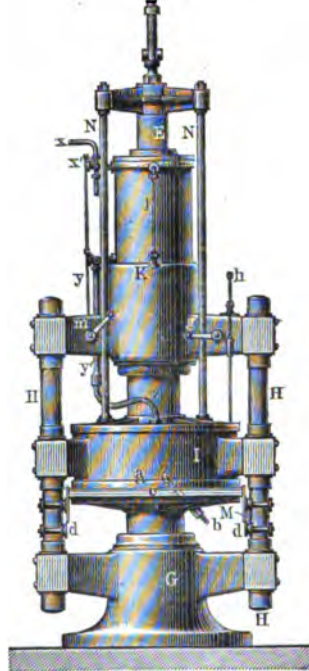


Fig. 44.



G carries two cylinders I and K, by means of the columns H H. The piston A, carrying the filter-plate L, is made to rise or descend by the introduction of water into the hollow space B. Plate L is provided with radial furrows, collecting the filtering-liquid in the annular spout *a*, from which it is carried outward by pipe *b*. The filter consists of sheet-iron covered with felt; the sheet-iron is square, and is only so far perforated as corresponds to the area of I; it is held in the frame *c*. When the bicarbonate cake has been pressed and washed, piston A is made to descend, whereupon frame *c* settles on the square frame M, which can be drawn out of the press on the eight guiding rollers *d*. The cake is then taken away, the filter is put back into its place, frame M is moved back into the press, and piston A is again raised.

The piston C, serving as compressor, is connected with piston E.

by four inflexible rods N. By the three-way cocks *e* and *f*, which are regulated by lever *m*, at the same time water is made to rise as required in the one or other of the cylinders F or D. In the former case, the water entering through pipes P and *r* lifts piston E. Piston C, which is also thus raised by means of the rods N, on rising produces a vacuum; hence the liquid to be filtered is aspirated, on opening valve *t'*, through pipe *t*. When piston E has reached the upper limit of its play, disk *u* touches the lever *v*, which turns the three-way cock *l* in such a manner that the connection between pipes P and *r* is closed, and that between P and O is opened; but as tap *f* is still closed, the movement is at once stopped. Now the attendant turns the crank *g*, and thereby makes communication between pipe *s* and cylinder D as well as between cylinder F and the outlet-pipe *r'*. Piston C sinks down and drives the liquid through the filter. When the pistons have arrived at the lower limit of their play, disk *x* touches lever *v*, and this regulates the valve *l* so that the communication between P and *s* is interrupted. The movement ceases, and while piston C' remains in its position, the bicarbonate cake is washed with pure solution of sodium carbonate. This arrangement acts quite automatically, and is not dependent upon the attention of the workmen.

The washings get through *x* and the three-way cock *x'* into the annular space O. They can be exactly measured by means of the water-gauge *l*. Now the man opens by means of crank *m* the taps *x* and *y*. Compressed air from a reservoir enters the space O, and drives the washings through tap *y* into pipe *y'*, connected with branch *z* by a thick india-rubber tube; *z* fits on a hole drilled in the bottom plate of piston C. The underside of this plate is provided with radial furrows, and is covered with sheet-iron and a filtering-cloth. The washing-liquor, forced on by the compressed air, enters through *z*, divides itself among the furrows and penetrates through the bicarbonate cake, to issue by branch *b*. Thus the cake is washed once or oftener before being taken out.

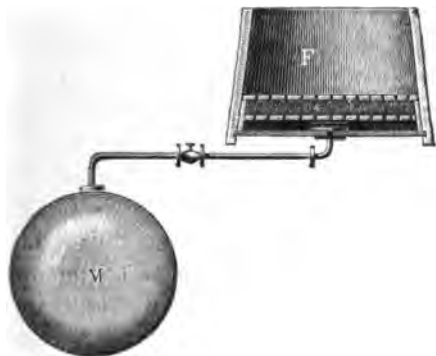
With a press of the indicated size, three cakes weighing 40 kil. each can be pressed per hour. One man superintends two presses at the same time. The bicarbonate loses 50 per cent. of its weight on calcining, hence the production is 120 kil. per man per hour.

Schreib (Chem. Zeit. 1890, p. 492) prefers as a filtering-medium, instead of cloth, a layer of limestone powder covered with white

sand and confined between two grids. Fig. 45 shows a wooden filter, connected at F with the pressure-valve M, which serves for several filters. (Such filters can only be used in small works.)

At other works the filtering of the bicarbonate is performed by *centrifugal machines* or by *filter-presses*. The former require too much motive power, and it is difficult to avoid losses and contaminations therein; the latter seem to have answered very well.

Fig. 45.



Fassbender (Zsch. f. angew. Ch. 1893, p. 259) gives a special calculation of the data for the vacuum filter-pump, from which we see that it requires 5 H.P. actually expended on the main shaft for a daily make of 10 tons soda-ash.

The rule, mentioned p. 74, that the bicarbonate must be obtained in a coarse granular form, not in that of fine mud, in order to be fit for filtering, obtains for all kind of apparatus, vacuum-filters, filter-presses, &c.

The bicarbonate remaining on the filters always contains some mother liquor, from which it must be freed by a thorough washing, as has already been described in the case of several apparatus. Especially the ammonia present as chloride or carbonate should be removed; but this can never be done entirely, as such a washing would dissolve too much sodium bicarbonate, which during the recovery of the  $\text{NH}_3$  is converted into  $\text{NaCl}$  and is thus lost. It is found difficult to dissolve any solid ammonium chloride. To remove this, Solvay proposed (p. 75) to heat up the bicarbonate with the washing-liquor, either at the bottom of the absorbing-tower by means of a steam-coil, or in a special apparatus outside.

It is of course impossible on washing the precipitate to avoid dissolving a certain quantity of the sodium bicarbonate, and his

is entirely lost, as on heating the mother liquor it is decomposed with the  $\text{NH}_4\text{Cl}$  into  $\text{NaCl}$  and ammonium bicarbonate. The loss by washing is scarcely below 10 per cent., and frequently above this. Schreib (Chem. Zg. 1889, p. 489) proposed to diminish it by employing mineral oil, in lieu of water, in order to remove the mother liquor mechanically without dissolving anything—of course only if there is no solid ammonium or sodium chloride present, whereas any solid ammonium bicarbonate would not do any harm, as it would be recovered on drying the sodium bicarbonate, together with the adhering mineral oil. [This proposal seems impracticable. Probably the loss of mineral oil would be too great, and the quality of the soda-ash would be hardly up to the mark.]

*The chemical examination of the crude bicarbonate is made as follows:—*First, the alkalimetric titre is established, then the percentage of  $\text{CO}_2$ , according to the methods indicated in Vol. II. pp. 112 and 629; also the percentage of ammonia by distilling with caustic soda and absorbing the distillate in standard acid; sometimes also the chloride, by neutralizing with nitric acid and titrating with silver nitrate (p. 32). The moisture is found by difference, but more directly by ascertaining the loss on ignition and deducting therefrom the second molecule of  $\text{CO}_2$ , and the ammonia (calculated as carbonate).

## II. *Drying and Calcining the Bicarbonate.*

Only a small portion of the sodium bicarbonate is sold as such, for which purpose it must be submitted to the treatment described in the 9th chapter. Most of it is converted into soda-ash, recently also into crystals or caustic soda. The task of converting the bicarbonate into monocarbonate and recovering the liberated  $\text{CO}_2$  and  $\text{NH}_3$  seems to be very simple, but in reality is very difficult, as is proved by the large number of patents taken out by Solvay and others for this operation, some of which we will describe, beginning with Solvay's patents.

In a vertical cylinder, G G (of which fig. 46 is a sectional elevation, and fig. 47 a sectional plan), there are a number of round plates H, with openings at the circumference and in the centre. A perpendicular shaft, I, passes through the top and bottom of the cylinder and carries arms K K, with scrapers L L, which move the mass lying on the plates alternately to the periphery of one and the centre of the next lower plate, so that it ultimately gets to the

Fig. 46.



Fig. 47.



bottom of the cylinder. The plates themselves are hollow and are heated by steam or hot gases. The bicarbonate is charged by a hopper M, in which arms O are slowly turned round by the shaft N; it is always kept full, so that the  $\text{CO}_2$  cannot escape. The dried mass arrives at the bottom of G in a finely-ground state, ready for packing. The gases driven off in drying escape by a pipe R in the top. If hollow plates are to be dispensed with, the gas can be conveyed directly into the cylinder. [It will be seen that this apparatus is quite similar to MacDougall's pyrites-small burners, Vol. I. p. 260. It is said not to work very well.]

Fig. 48.

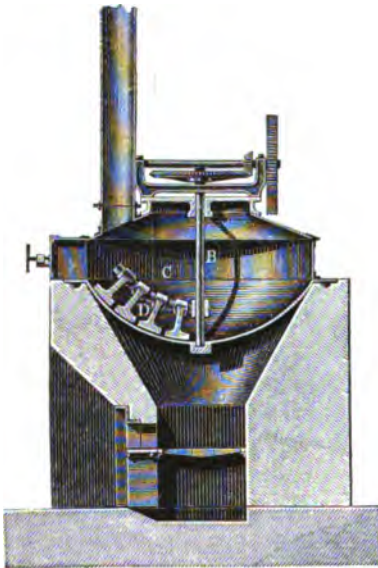


Fig. 49.



Fig. 50.



Fig. 51.



Another drying-apparatus for soda is shown in figs. 48 and 49; it consists of an iron pan A, closed by a cover through which a perpendicular shaft B passes in a gland. The latter carries arms C, with scrapers D, which stir round the bicarbonate, the pan being heated to the proper degree by a fire below. The most recent construction of scrapers is shown in figs. 50 and 51: c is the scraper itself, which has a certain amount of play round the revolving shaft B; S is the surface to be scraped; and the arrow F shows the direction in which the scrapers move.

According to patent 2143, 1876. Solvay separates the decomposition of the bicarbonate from the calcining of the soda-ash. The former he performs either by means of steam with an apparatus to be described further on, but evidently only intended for such cases in which a *solution* of sodium carbonate is required for the manufacture of soda crystals or caustic, or else he employs chemical means for removing the second molecule  $\text{CO}_2$ , viz. pressing ammonia gas through the mass or soaking it with ammoniacal brine, both at a higher temperature. [This does not seem to have been practically applied.]

Fig. 52.

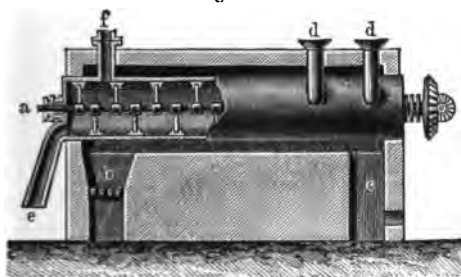


Fig. 52 shows a more recent drying-apparatus, patented by Solvay in 1879. A horizontal cast-iron cylinder, provided with an agitating-shaft *a*, is heated all round by the flame coming from the grate *b*; *c* is the exit-flue for the fire-gas. The moist bicarbonate is introduced by the lateral charging-funnels *d, d*, which are always kept full, so as to prevent any escape of gas in this place. The calcined mass is discharged through the pipe *e*, reaching nearly to the bottom; steam,  $\text{NH}_3$ , and  $\text{CO}_2$  escape through *f*. The scrapers attached to shaft *a* move the salt towards the fire end and prevent it from caking to the sides of the cylinder. The vapours escaping by *f* are cooled, to condense the steam and most of the ammonia (as bicarbonate); the remaining  $\text{CO}_2$  is pumped away, together with a little  $\text{NH}_3$ , and is pumped into the carbonating-tower in a place where normal ammonium carbonate is already formed and is thus converted into bicarbonate.

Unger (Germ. pat. 10392) describes a similar apparatus, consisting of a horizontal retort with a carrying-screw (creeper).

The German patents Nos. 16181 and 23190 of Solvay prescribe mixing some dry soda with the moist bicarbonate, in order to

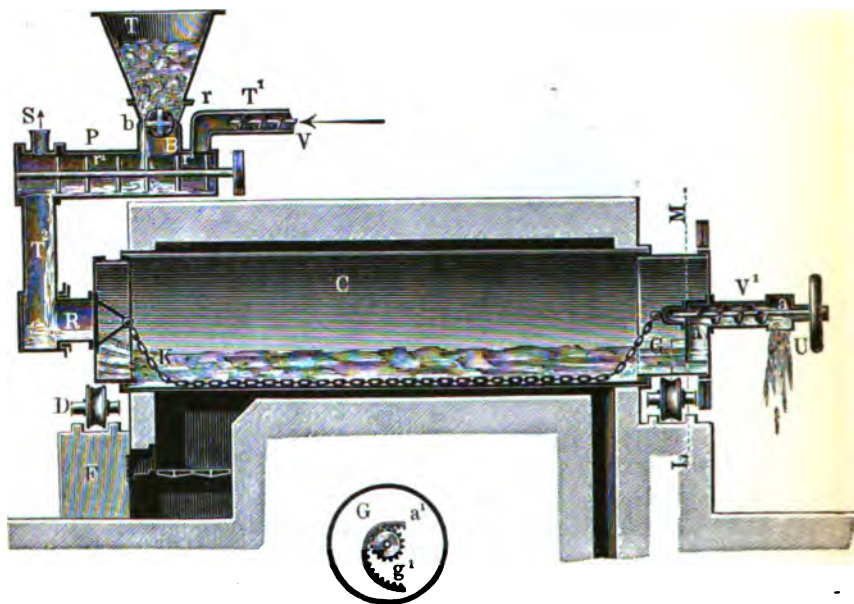


prevent its clogging the agitating-gear, and describe an apparatus intended to perform this mechanically.

Mond (Eng. pat. 716, 1883) returns to a circular pan with agitating-gear and cover.

In 1887, Solvay again patented an apparatus intended for a mixture of moist bicarbonate and dry soda-ash (Eng. pat. 13323, 1887). This is shown in fig. 53. A wrought-iron or cast-iron

Fig. 53.



drum C is placed on rollers D above a fireplace F, and is kept revolving. Within the charging-funnel T there is a propeller b, moving the damp bicarbonate from B to P, and preventing any gas from escaping here. At the same time dry hot soda-ash from the exit end of the cylinder is charged into P through T¹ and the propeller V, and is mixed by the propeller r¹ with the damp bicarbonate. Propeller V does not quite reach to the elbow r, so that some soda-ash accumulates there and forms a gas-tight lute. Through the drop-tube T² and the box R the mixture gets into the calcining-drum C. From this the calcined mass is lifted out by the scoop G, which is fixed at the bottom of the drum, moves



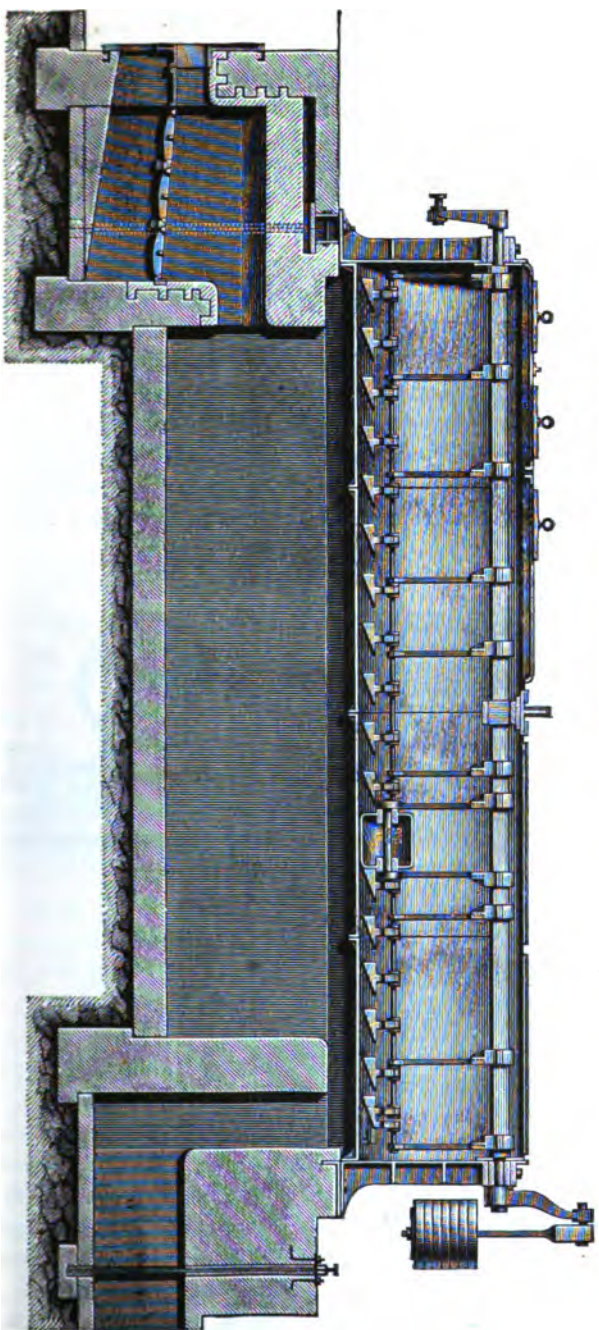
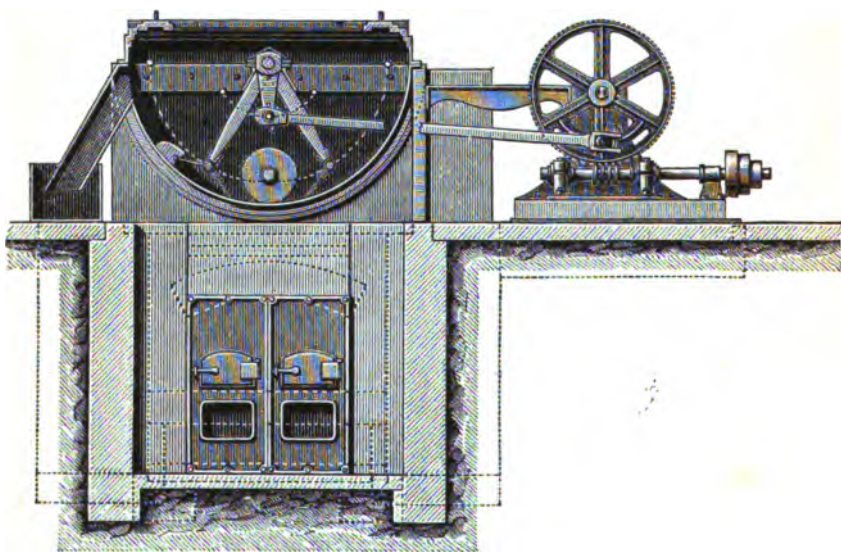


Fig. 64.

in the same direction, takes up some soda-ash at each revolution and throws it against the shaft *a*, whose teeth, together with the teeth on the inside of *G*, crush the lumps. Propeller *V*<sup>1</sup> turns in the opposite direction to the drum and moves the scooped-out ash towards the discharging-tube *U*; it does not quite reach to the mouth of *U*, so that here also a plug of soda-ash is formed, which keeps the furnace gas-tight at this place. The vapours escape through the branch-tube *S*, fixed on *T*<sup>2</sup>. The heavy drum *K* prevents the formation of crusts within *C*.

Solvay's apparatus, shown in fig. 52, is on principle exactly similar to Thelen's drying-apparatus; constructed for Leblanc soda (Vol. II. p. 662, Eng. pat. 4747, 1879). The latter has been adopted by most ammonia-soda works, including Solvay's own, with the modification of closing the top by a cover and providing an outlet-pipe for the vapours. This form is shown in figs. 54

Fig. 55.



and 55. With Thelen pans the work can be continued up to driving out all the bicarbonate  $\text{CO}_2$ , thus producing finished soda-ash, which needs no grinding and is of very good colour, as it contains no dust from fireplaces; but it is very porous, which causes some drawbacks, to be subsequently mentioned, and the apparatus also

suffers a good deal if the calcining is driven up to this point (comp. *infra*).

The Thelen pans are mostly from 7 to 8 feet wide and about 30 feet long; they are composed of several pieces of cast-iron and are covered at the top to collect and utilize the gas. The heating is produced by an ordinary fireplace at the end opposite to the entrance of the damp bicarbonate. The agitating-gear has an oscillating movement, and causes not merely the sides of the pan to be kept free from crusts, but also moves the mass slowly towards the fire end, where it is discharged in the dry state. With sufficient care in keeping the cover tight and avoiding any unnecessary opening of the man-holes, gas containing from 60 to 80 %  $\text{CO}_2$  can be obtained here, whereas in the ordinary drying-apparatus the gas tests only 50 %, and in that used a number of years ago only 25 %  $\text{CO}_2$ , owing to the admixture of air. According to the size of the pan and the percentage of moisture in the bicarbonate one pan produces from 7 to 15 tons of soda-ash in 27 hours, with an expenditure of 20 or 25 % of coal. The larger they are, the better they work. The product is fit for packing at once, unless dense soda-ash is required.

Usually the drying in all the apparatus hitherto described is not carried to the point that all the  $\text{NaHCO}_3$  is converted into  $\text{Na}_2\text{CO}_3$ ; this would require too much time, fuel, and wear and tear of the apparatus, which would not be covered by the small gain of carbonic acid. Usually the process is continued only up to the point where the whole of the ammonia is sure to be driven off, at which point about 25 per cent. of the bicarbonate is still undecomposed. The last calcining is performed in a reverberatory furnace, which takes less fuel and yields denser soda than the direct finishing in closed apparatus heated from without. The Solvay works now proceed in this manner: first drying in Thelen pans up to the degree just mentioned and afterwards, if needful, calcining by open fire in Mactear furnaces.

The apparatus described in the following pages are seldom, if ever, used, even at the Solvay works.

In one of his patents Solvay employs for the final calcining, after previously drying, a cylindrical furnace somewhat inclined (figs. 56 and 57), consisting of an iron shell and a brick lining which is slowly turned round by the cog-wheels E and e; it is supported on friction-rollers r and r'. F is a kind of gas-generator;

Fig. 57.

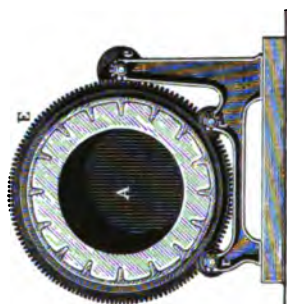
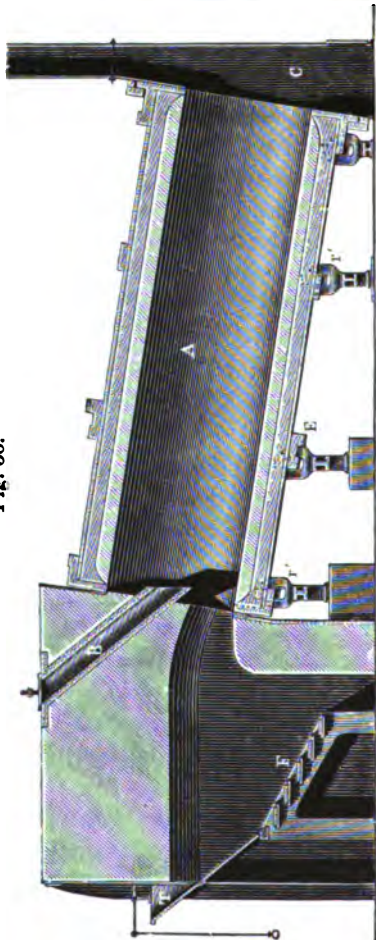


Fig. 58.



T, the hopper for introducing coals; B, the pipe for supplying the bicarbonate; C, chamber for collecting the calcined soda-ash.

At the Northwich works the bicarbonate was in 1878 first subjected to a comparatively low temperature in a closed roaster, within which a perpendicular shaft revolved with horizontal arms and scrapers sweeping its bed; but the operation was always finished in other closed roasters (muffle-furnaces), where the soda-ash was brought to a bright-red heat by gaseous fuel. Thus it becomes much denser than that finished at a low temperature. By mechanical pounding in the casks it becomes still denser, but never quite so dense as calcined ash made by Leblanc's process.

Solvay afterwards patented (No. 2687, 1877) the following process for obtaining soda-ash in a dense form for melting-operations:—The damp bicarbonate is continuously or gradually put into the funnel E (fig. 58), and from this gets into the trough C. Here some monocarbonate is formed.  $\text{CO}_2$ ,  $\text{NH}_3$ , and steam are conveyed away by the pipe T. The shaft A, moved by a cog-wheel, carries two arms F F, to which the scrapers R are attached on a swivel-joint; these prevent the sticking of the mass to the trough. While the soda is descending in the retort G, it is heated up to the melting-point, and can be run off through the openings O and O'. When it runs off through the opening O', the impurities settle in front of the lower opening O, and can be removed through it. H is the fire-grate; I and K, smoke-flues.

Figs. 59 and 60 show another arrangement of the apparatus, in which the retort has a different shape, and is provided with the pipe *t* for running off the soda. *b b* are fire-bricks distributing the flame to make the temperature of the apparatus more uniform. Fig. 61 shows an apparatus working without machinery. The soda or bicarbonate is put into the hopper E, till the vessel C is filled. The melted mass runs off through *t*;  $\text{NH}_3$  and  $\text{CO}_2$ , along with steam, escape by T. Within C the bell X can be placed, in order to diminish the thickness of soda to be heated. The vessels for melting the soda can be made of cast or wrought iron, steel, or other metal, and protected against the oxidizing action by a coating of fireclay or a paint of borax solution &c.; or the non-oxidizing flame of a Siemens furnace may be employed; or the part of the apparatus in which the soda is melted may be made of silver or silvered.



Fig. 58.

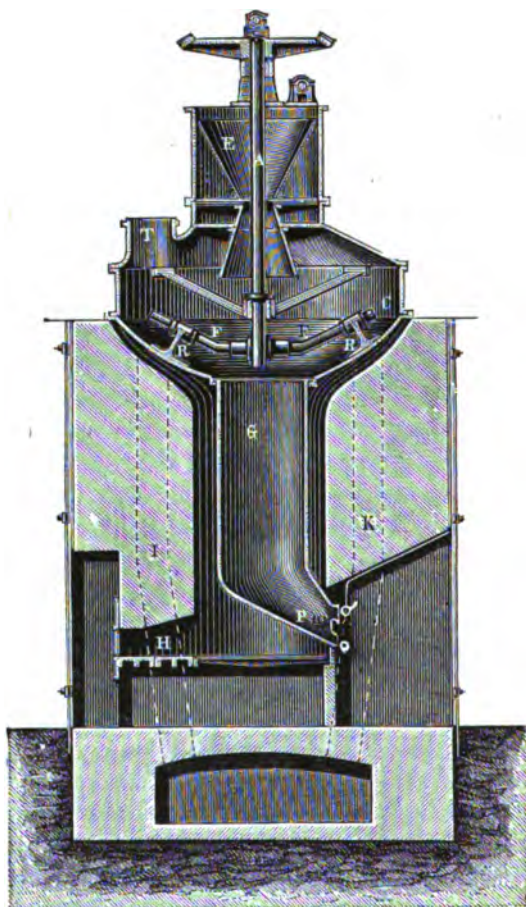


Fig. 59.

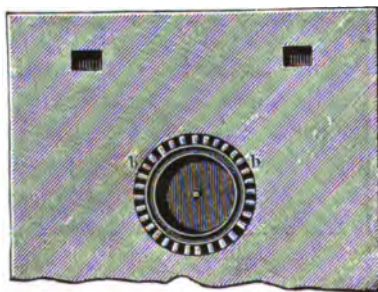
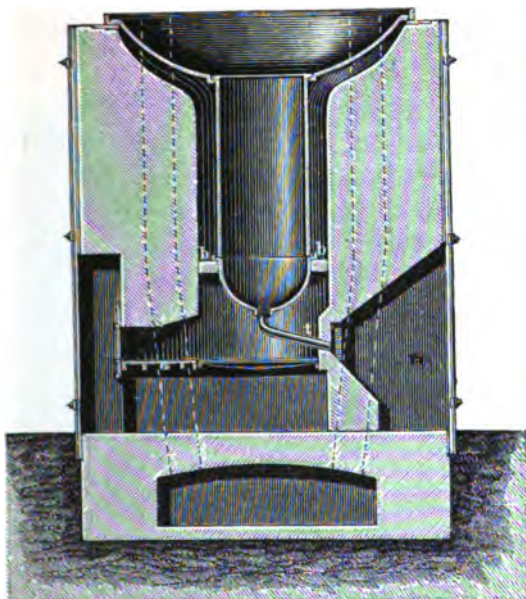


Fig. 60.

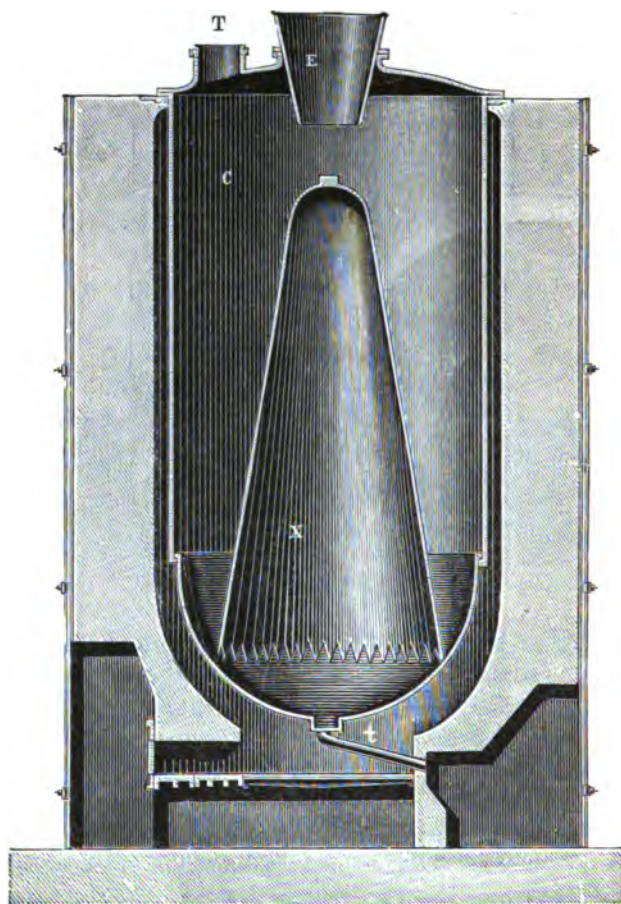


The simplest plan for cooling the soda run out is by squirting as little water upon it as will evaporate at once without being absorbed by the soda. If it is to be granulated, it is run upon a revolving metal plate, and at the same time a small jet of water (as just mentioned) is run upon it.

In order to make soda-ash containing a little caustic (similar to the "sels caustiques" of French works), a steam-jet is forced through the melted soda or upon its surface. This expels some  $\text{CO}_2$  and generates  $\text{NaOH}$ , which can be continued up to the desired point; in the continuous apparatus the steam-jet must be continuous as well, and regulated according to the degree of causticity desired. The steam-pipe is shown in fig. 58 at P; its end is perforated with small holes. When employing the apparatus fig. 60 or 61, the soda is best first run into a vessel, where it is kept in the liquid state, and there treated by steam.

In order to make soda of weaker strength, Solvay soaks it with brine before drying it; or a sufficient quantity of water is incorporated with it by contact at the ordinary temperature. [In many cases neither of these plans are feasible.]

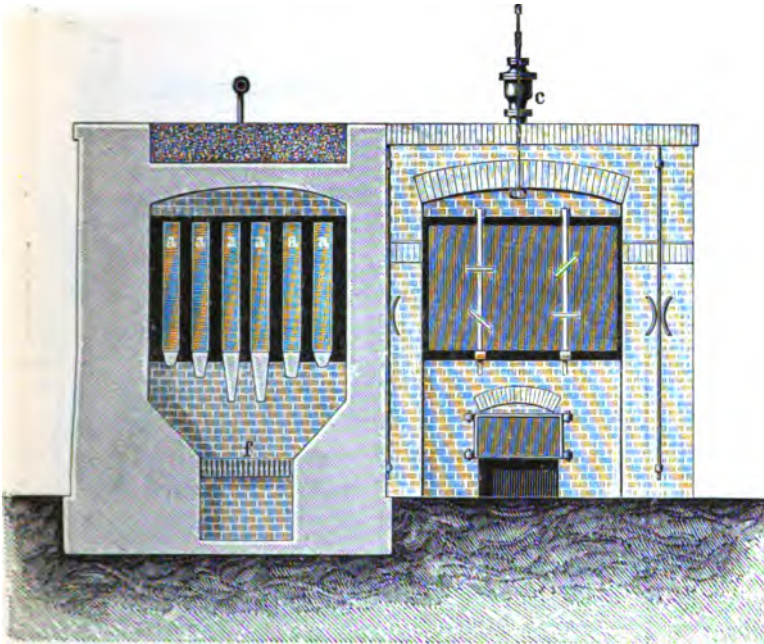
Fig. 61.



Boulouvard's calcining-apparatus (French pat. 114852, 1876) is shown in figs. 62 and 63 on a scale of 1 : 30. It consists of a set of cast-iron retorts *a, a*, rectangular in section, 4 in. wide and 1 ft. 8 in. high, with a common head B. Each retort receives two sheet-iron boxes *c* and *d*, with perforated sides. The flame coming from the fireplace *f* entirely surrounds the retorts *a, a*; the escaping steam and carbonic acid arrive first in the head B, then escape through the pipe *c*, provided with a valve, and get into the lead cooling-worm *r*. Each of the 12 boxes *c, d* receives a



Fig. 62.

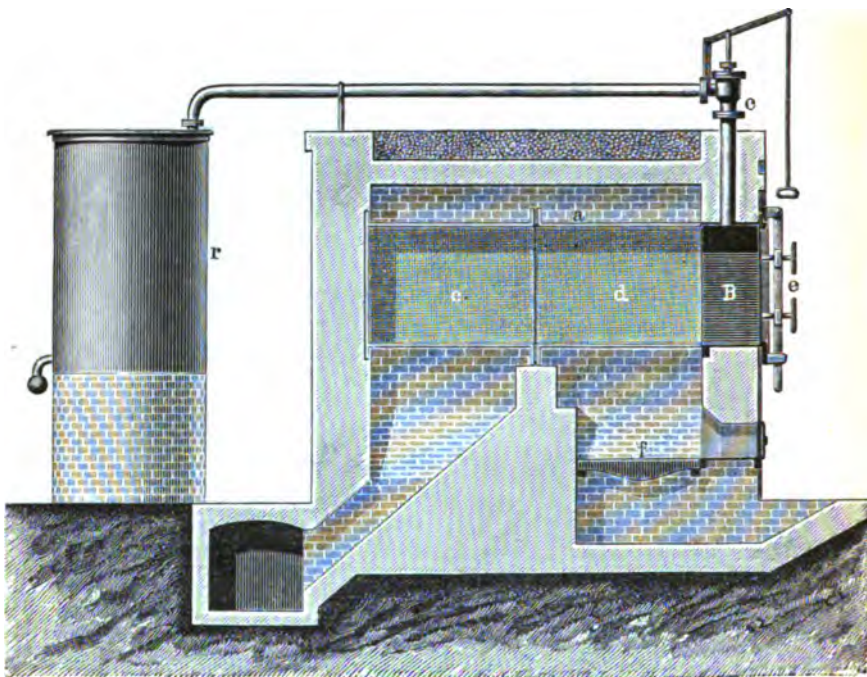


charge of 20 kil. bicarbonate. The calcining lasts about six hours; then the door *c* is opened, the boxes are drawn out by means of an iron hook and are emptied in the warehouse.

Mond (Engl. pat. 716, 1883) employs a combination of a mechanical muffle-furnace and a reverberatory furnace. In the first  $\text{NH}_3$  and  $\text{CO}_2$  are driven out, in the second the calcining is finished.

Honigmann (Germ. pat. 13782) calcines the bicarbonate by hot lime-kiln gas, which is thereby made richer in  $\text{CO}_2$  and receives some  $\text{NH}_3$ . [This process seems useless, as the soda-ash must be too much contaminated with dust drawn from the lime-kilns; if that dust is to be removed, recourse must be had to washing, and this cools the gas!] About the same time Péchiney patented the same thing (Engl. pat. 2099, 1880), and this was repeated much later by Gossage (Engl. pat. 15822, 1891). Péchiney states that by this process the soda-ash is obtained in a more granular state than usual.

Fig. 63.



Herberts (Engl. pat. 8617, 1884) describes an apparatus for this object in which the removal of the  $\text{CO}_2$  is to be effected by methodical treatment in five cylinders, provided with agitating-gear, mounted terrace-wise, and heated by open fire or steam.

Schüchtermann and Kremer (Germ. pat. 61349) employ a set of semi-cylindrical troughs, mounted on a common block of brick-work in such manner that the conveying-blades revolving therein both agitate the mass and throw it from one vessel into the other.

La Société Marcheville Daguin et Cie. (Engl. pat. 12997, 1893) describes a revolving furnace with vertical axis for the same purpose.

Bell (Engl. pat. 13708, 1893) employs a retort in which superheated steam is made to decompose the moist bicarbonate into  $\text{Na}_2\text{CO}_3$  and almost pure  $\text{CO}_2$ , which is again used after condensing the water by cooling.

Rube (Germ. pat. 13,430) describes a continuous calciner, indirectly fired, somewhat similar to Solvay's first drying-apparatus (p. 82).

A similar apparatus is Frasch's shelf-furnace with mechanical stirrers, cooled by water, which I have described in *Zsch. f. angew. Chem.* 1894, p. 15, as a roasting-furnace for sulphides. For the present purpose it must of course be provided with a special fire, preferably a gas-producer, or else it is heated by liquid fuel injected in the form of a spray.

Matheson and Hawliczek (Engl. pat. 5753, 1887) propose to make denser soda-ash than usual with ammonia-soda. Their apparatus consists of a cylinder heated from below, in which the mass is mechanically stirred and moved from one end to the other. It is very long, so that the conversion into normal carbonate is finished about the middle of its length. In this place a spray of water or a jet of steam is injected, which makes the mass granular and dense; at the other end it runs out into a discharging-shoot leading to the mill.

At most works, where the salt coming from Thelen pans is to be made denser, a Mactear carbonating furnace is employed, as is described and illustrated in Vol. II. p. 677. By this ammonia-soda can be brought to a density of 1.0, that is 70 lbs. per cubic foot, which is near enough to that of Leblanc soda, although not quite equal to it (comp. Vol. II. p. 110). At the Solvay works all the salt is first dried in Thelen pans; that portion of it which has to be made denser is then carried by a mechanical elevator into Mactear furnaces, and is there calcined with mechanical stirring (p. 89). It is then fit for over-sea carriage or other special uses of dense soda-ash.

*Consumption of Fuel in Calcining.*—In the case of closed apparatus coal is used for firing; Mactear furnaces and other open furnaces must be fired with coke. Schreib (*Chem. Zeit.* 1890, p. 493) states the consumption of coke as 15 parts for 100 soda-ash.

*Treatment of the escaping Vapours.*—All apparatus for the first treatment of bicarbonate (excepting the open furnaces intended to produce the final degree of density) must be closed, to utilize the escaping carbonic acid and ammonia. Any  $\text{NH}_4\text{Cl}$  present at first is in this process converted into ammonium carbonate, which escapes, split up into  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . These three are therefore the components of the escaping gases, together with a little

air. They are first cooled down by any suitable means, *e. g.* tubular coolers flushed with water outside, in which a solution of ammonium carbonate is condensed. The gases then pass through a scrubber, in which they yield the remainder of their  $\text{NH}_3$  to water. After this comparatively pure carbonic acid is left, which is forced, by the same pump which has aspirated the vapours, from the drying apparatus and through the coolers and scrubbers into the carbonators, preferably at a place where ammonium carbonate is already formed and is to be further transformed into bicarbonate (pp. 59, 66, &c.).

Fassbender (*Zsch. f. angew. Ch.* 1893, p. 260) gives a detailed calculation, according to which the vacuum-pump for the calcining-pans requires 10 effective H.P. for a production of 10 tons soda-ash per day.

The ammoniacal liquors, obtained by the above-mentioned coolers and scrubbers, are returned to the ammonia-stills, unless they can be employed for dissolving salt or purifying brine (p. 22). They are best treated in a special still which serves only for these weak liquors. It has not been found advantageous to leave the  $\text{NH}_3$  in the  $\text{CO}_2$  gas and use this directly for the carbonating process, probably because losses occur during the transit through a long string of pipes.

#### *Cooling and Packing the Soda-ash.*

At large factories the cooling of the soda-ash, as it comes from the calciners, would take too much time and space in the warehouse before it could be transferred to the mills or packages. Therefore *mechanical coolers* are employed, consisting of an endless carrying plane, composed of iron plates cooled by water from below; they receive the hot stuff from the calciner at one end and deliver it cooled down at the other end to the *mills*, as described in Vol. II. p. 688.

Ammonia-ash is *packed* partly in casks, as in the case of Leblanc ash (Vol. II. p. 689), and partly in bags, which are much cheaper and well adapted for inland transit.

### *III. Manufacture of Caustic Soda and Soda Crystals directly from Bicarbonate without Calcining.*

Drying or calcining apparatus for the crude bicarbonate is unnecessary where it is not intended to sell the finished product as

soda-ash, but in the shape of caustic or crystals, where it is requisite to prepare first a solution of soda. In these cases the moist washed carbonate can be treated in the state of a paste with steam, preferably with mechanical stirring; the escaping mixture of steam, ammonia, and carbonic acid is cooled down, to condense a solution of ammonium carbonate, and the remaining  $\text{CO}_2$ , containing a little  $\text{NH}_3$ , is used over again in the process. From the paste a solution is formed containing mostly normal sodium carbonate, which can be worked up into soda crystals or caustic soda. Much steam is used in this process, and the question whether this is cheaper than drying in a Thelen pan and re-dissolving will be decided differently in different places. At all events, the Solvay works proceed in the first-described manner.

It is practically impossible to expel the bicarbonate-carbonic acid completely by merely boiling the liquor; this, at all events, would cost too much time and steam. If caustic soda is to be manufactured it is usual to boil till about three-fourths or four-fifths of the alkali is present as normal carbonate, and only one-fourth or one-fifth is left as  $\text{NaHCO}_3$  (comp. Vol. II. p. 745). This, of course, involves a considerably larger consumption of lime than with Leblanc ash, and even a larger excess in comparison with the use of crude Leblanc tank-liquor, which contains much  $\text{NaOH}$  to begin with. This circumstance not merely increases the expense for lime, but it also causes more loss through the formation of gaylussite (Vol. II. p. 754), which must be taken into account when drawing up estimates of cost.

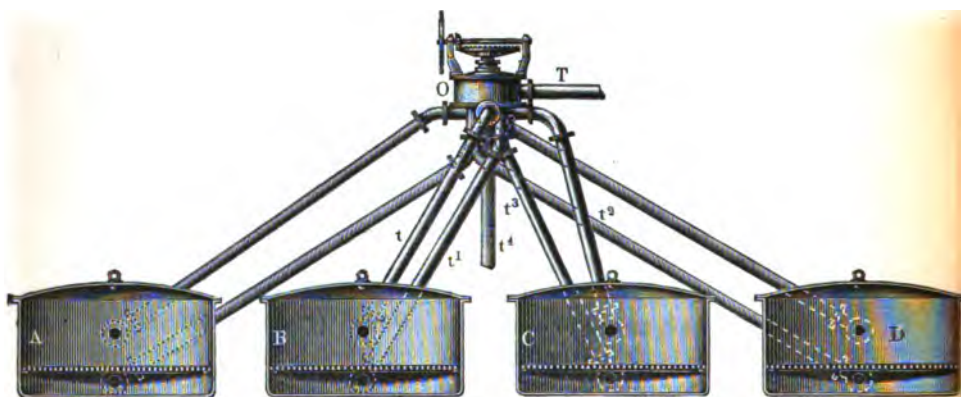
An estimate of the materials and costs in manufacturing caustic soda from ammonia-soda has been given Vol. II. p. 808.

For *crystal soda* the liquor directly obtained by boiling cannot be immediately employed; in the presence of bicarbonate, even in small quantity, small pointed crystals are formed in lieu of the large crystals required in trade. The bicarbonate must be first removed by adding some caustic soda or by lime. To obtain large hard crystals it is necessary to add about 2 or 3 per cent. sodium sulphate of the weight of the sodium carbonate; this also holds good when manufacturing crystal soda from calcined ammonia-soda (comp. Vol. II. p. 704).

A complete removal of the bicarbonate in making crystals from ammonia-soda does not seem to be either necessary or usual. At

least crystals of urao (four-thirds carbonate) have been found by Cl. Winkler in mother liquors of the Ebensee ammonia-soda works (Zsch. f. angew. Chem. 1893, p. 446).

Fig. 64.



In Solvay's Engl. pat. 2173, 1876, an apparatus is described for the above purpose, as shown in fig. 64. A, B, C, D are the decomposing-vessels, O a distributor supplied with steam through T, which admits of putting one or more of the vessels A to D out of turn for emptying and refilling. If, *e. g.*, A is to be emptied and D to be filled, steam is sent from O through *t* into the upper part of B, where it penetrates through the bicarbonate, issues at *t¹*, again enters the distributor, leaves this at *t²*, enters again through *t³*, and finally escapes at *t⁴* into the top of the ammonia-still, where its CO<sub>2</sub> is utilized. The heat of the steam suffices for decomposing the bicarbonate; the water condensing there assists by the latent heat being liberated during its liquefaction. The liquor running away is employed for the first lixiviation of the crude bicarbonate on the filters.

Abel (Engl. pat. 3656, 1883) patents the manufacture of soda crystals from bicarbonate in the way just described; also H. Gaskell (No. 4274, 1886).

Hawliczek (No. 9425, 1885) proceeds in the same way, but the solution obtained, which is coloured greenish by tarry substances, is treated with chlorine water, and then on cooling yields perfectly white crystals. His apparatus consists of a

cylindrical vessel with conical bottom; steam enters just above the lowest point through a bell nicked out at the bottom; above this is a journal for the agitating-gear, consisting of two spiral blades wound in opposite directions. On boiling at the ordinary pressure the decomposition does not exceed 40 per cent.; it must therefore be completed by high-pressure steam and agitation.

Campbell, Boyd, and Kirkpatrick (No. 21,071, 1890) again patent boiling in aqueous solution of bicarbonate with steam, in order to work up the remaining liquid for caustic soda. As an alternative for the use of steam they mention hot lime-kiln gas for decomposing the bicarbonate. [This will hardly work, on account of the impurity of lime-kiln gas.]

Staub (Engl. pat. 7859, 1887) describes the *conversion of an aqueous solution of sodium bicarbonate into monocarbonate by ammonia*. On heating a solution of  $\text{NaHCO}_3$  with ammonia, ammonium carbonate, or sulphide, the  $\text{CO}_2$  combined with the  $\text{NH}_3$  is drawn off in the gaseous form, while the  $\text{NH}_3$  remains behind, withdraws more  $\text{CO}_2$  from the  $\text{NaHCO}_3$ , and thus finally leaves  $\text{Na}_2\text{CO}_3$  behind. This is promoted by pressure. The inventor makes bicarbonate solution with a solution of ammonia at  $60^\circ \text{C}$ . in a cylinder, exactly similar to the old ammonia-saturator described by Solvay (fig. 3, p. 26), provided with an inner steam-coil and agitating-gear, and pumps the solution into a column, consisting of a Solvay tower combined with an ammonia distilling-column. The solution runs in at the top; steam and ammonia enter at the bottom. Higher up, as already mentioned, ammonium carbonate is formed, as well as sodium monocarbonate; the former on descending is again split up into  $\text{CO}_2$ , which escapes as a gas, and free  $\text{NH}_3$ , which in the hottest place, near the bottom, is equally expelled, so that the solution leaving the tower contains nothing but pure  $\text{Na}_2\text{CO}_3$ . If once the whole process is in proper order, only so much  $\text{NH}_3$  must be introduced as is required for covering any loss of it. At the top the  $\text{CO}_2$  escapes and is, as usual, purified from steam and ammonia by a tubular condenser.

By a similar method (Engl. pat. 8129, 1887) Staub proposes precipitating from solutions of sodium carbonate by means of ammonia certain *hydrates* of sodium carbonate, differing according to the temperature and pressure employed.

## CHAPTER VI.

## RECOVERY OF THE AMMONIA.

THE mother liquors and washings running from the bicarbonate filters contain most of the ammonia, viz. everything except that recovered in the washers for the gases escaping from the various apparatus. The greater portion of the ammonia is present in the mother liquors as chloride, but an essential portion of it, say 15 or 20 per cent. (comp. p. 71), in the state of bicarbonate. In other words, the sodium bicarbonate present with the ammonium chloride in the mother liquor, on heating the liquor, decomposes into ammonium chloride and ammonium bicarbonate\*. Apart from this the liquor, of course, contains the whole of the sodium chloride which has escaped the principal reaction, and this is augmented by that formed in the reaction between  $\text{NH}_4\text{Cl}$  and  $\text{NaHCO}_3$ .

The *chemical analysis* of the mother liquors up to the stage of distillation embraces the estimation of free and fixed  $\text{NH}_3$ , as described on p. 32; also that of the undecomposed  $\text{NaCl}$ . The latter is performed by evaporating 10 c. c. in a platinum capsule, igniting till all  $\text{NH}_4\text{Cl}$  has been volatilized, and weighing.

Since the ammonia-soda makers must compensate the inevitable manufacturing loss of ammonia by a fresh supply, and since this is regularly done by passing the commercial ammonium compounds through the stills, together with the mother liquors from the process, we will treat of the fresh supply in this place.

Ammonia is commercially procurable either in the shape of crude *gas-liquor*, or of *concentrated gas-liquor*, or of solid *sulphate of ammonia*. Concerning the origin, preparation, and properties of these substances, I refer the reader to my 'Coal-tar and Ammonia'

\* According to the modern theories of electrolytic dissociation, most of the salts are split up into free ions; but it is the less needful to discuss this, as in such concentrated solutions there must be also undissociated molecules of the salts.

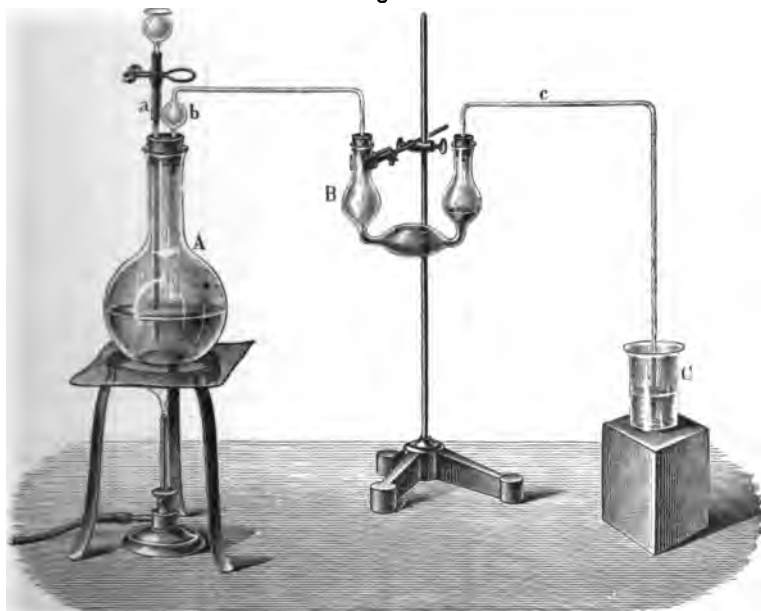


(2nd edition, 1887). Here I simply quote the testing methods for those commercial products, and these only so far as they are of interest for the present purpose.

The crude or concentrated *gas-liquor* contains the  $\text{NH}_3$  principally as carbonate, also partly as sulphide (*volatile ammonia*), much less as chloride, sulphocyanide, thiosulphate, ferrocyanide, &c. (*fixed ammonia*), which compounds give up the  $\text{NH}_3$  only on boiling with alkali or lime. For our purpose we require merely the following tests:—

1. *Volatile Ammonia*.—Dilute 20 c. c. gas-liquor with 10 c. c. water, add 30 c. c. normal hydrochloric acid, boil till all  $\text{CO}_2$  and  $\text{H}_2\text{S}$  has been expelled, and titrate back with semi-normal soda solution, employing the ordinary indicators. In case of strongly coloured liquor it must be diluted, or the point of neutrality must be found by means of litmus-paper. Each c. c. normal acid is = 0.017 grm.  $\text{NH}_3$ , or 20 c. c. = 0.085 per cent. in 100 vols., or = 0.4216 ounces of strong vitriol (93 per cent.) per gallon.

Fig. 65.



2. *Total Ammonia*.—Place 20 c. c. gas-liquor into flask A (fig. 65), together with 20 c. c. water; put 30 c. c. normal acid, diluted to

60 c. c., into the receivers B and C, B receiving the principal portion. Then run in an excess of milk of lime through the tap *a*, boil for one or two hours to drive all  $\text{NH}_3$  into B, unite the contents of B and C, and titrate back with semi-normal soda solution.

If *a* indicates the number of c. c. of the latter,  $30 - \frac{a}{2}$  shows the

1.—SPECIFIC GRAVITIES OF LIQUOR AMMONIÆ AT 15° C.

(Lunge and Wiernik.)

Specific Gravity at 15°.	Per cent. $\text{NH}_3$ .	1 litre contains grms. $\text{NH}_3$ .	Correction of the Specific Gravity for $\pm 1^\circ \text{C}$ .	Specific Gravity at 15°.	Per cent. $\text{NH}_3$ .	1 litre contains grms. $\text{NH}_3$ .	Correction of the Specific Gravity for $\pm 1^\circ \text{C}$ .
1.000	0.00	0.0	0.00018	0.940	15.63	146.9	0.00039
0.998	0.45	4.5	0.00018	0.938	16.22	152.1	0.00040
0.996	0.91	9.1	0.00019	0.936	16.82	157.4	0.00041
0.994	1.37	13.6	0.00019	0.934	17.42	162.7	0.00041
0.992	1.84	18.2	0.00020	0.932	18.03	168.1	0.00042
0.990	2.31	22.9	0.00020	0.930	18.64	173.4	0.00042
0.988	2.80	27.7	0.00021	0.928	19.25	178.6	0.00043
0.986	3.30	32.5	0.00021	0.926	19.87	184.2	0.00044
0.984	3.80	37.4	0.00022	0.924	20.49	189.3	0.00045
0.982	4.30	42.2	0.00022	0.922	21.12	194.7	0.00046
0.980	4.80	47.0	0.00023	0.920	21.75	200.1	0.00047
0.978	5.30	51.8	0.00023	0.918	22.39	205.6	0.00048
0.976	5.80	56.6	0.00024	0.916	23.03	210.9	0.00049
0.974	6.30	61.4	0.00024	0.914	23.68	216.3	0.00050
0.972	6.80	66.1	0.00025	0.912	24.33	221.9	0.00051
0.970	7.31	70.9	0.00025	0.910	24.99	227.4	0.00052
0.968	7.82	75.7	0.00026	0.908	25.65	232.9	0.00053
0.966	8.33	80.5	0.00026	0.906	26.31	238.3	0.00054
0.964	8.84	85.2	0.00027	0.904	26.98	243.9	0.00055
0.962	9.35	89.9	0.00028	0.902	27.65	249.4	0.00056
0.960	9.91	95.1	0.00029	0.900	28.33	255.0	0.00057
0.958	10.47	100.3	0.00030	0.898	29.01	260.5	0.00058
0.956	11.03	105.4	0.00031	0.896	29.69	266.0	0.00059
0.954	11.60	110.7	0.00032	0.894	30.37	271.5	0.00060
0.952	12.17	115.9	0.00033	0.892	31.05	277.0	0.00060
0.950	12.74	121.0	0.00034	0.890	31.75	282.6	0.00061
0.948	13.31	126.2	0.00035	0.888	32.50	288.6	0.00062
0.946	13.88	131.3	0.00036	0.886	33.25	294.6	0.00063
0.944	14.46	136.5	0.00037	0.884	34.10	301.4	0.00064
0.942	15.04	141.7	0.00038	0.882	34.95	308.3	0.00065

normal acid consumed, which is expressed in terms of  $\text{NH}_3$ , as in No. 1.

In the case of *concentrated* gas-liquor less of it is taken for analysis, or more acid is put into the receivers.

*Sulphate of Ammonia.*—A good average sample is taken, triturated, sifted, and well mixed. Of this 1·7 gram is put in flask A (fig. 65) (weighing 17 grams, dissolving to 500 c. c., and employing 50 c. c. for each test) and distilled with caustic soda. Each c. c. of the quantity of normal acid  $\left(\frac{30-a}{2}\right)$  shows 0·017 gram = 1 per cent.  $\text{NH}_3$ .

## 2.—SPECIFIC GRAVITIES OF SOLUTIONS OF COMMERCIAL AMMONIUM CARBONATE AT 15° C.

(Lunge and Smith.)

Deg. Twaddell.	Deg. Baumé.	Spec. Gravity at 15°.	Per cent. Com- mercial Ammonium Carbonate.	Change of Spec. Gravity for $\pm 1^\circ \text{C}$ .
1	0·6	1·005	1·66	0·0002
2	1·4	1·010	3·18	0·0002
3	2·1	1·015	4·60	0·0003
4	2·7	1·020	6·04	0·0003
5	3·4	1·025	7·49	0·0003
6	4·1	1·030	8·93	0·0004
7	4·7	1·035	10·35	0·0004
8	5·4	1·040	11·86	0·0004
9	6·0	1·045	13·36	0·0005
10	6·7	1·050	14·83	0·0005
11	7·4	1·055	16·16	0·0005
12	8·0	1·060	17·70	0·0005
13	8·7	1·065	19·18	0·0005
14	9·4	1·070	20·70	0·0005
15	10·0	1·075	22·25	0·0006
16	10·6	1·080	23·78	0·0006
17	11·2	1·085	25·31	0·0007
18	11·9	1·090	26·82	0·0007
19	12·4	1·095	28·33	0·0007
20	13·0	1·100	29·93	0·0007
21	13·6	1·105	31·77	0·0007
22	14·2	1·110	33·45	0·0007
23	14·9	1·115	35·08	0·0007
24	15·4	1·120	36·88	0·0007
25	16·0	1·125	38·71	0·0007
26	16·5	1·130	40·34	0·0007
27	17·1	1·135	42·20	0·0007
28	17·8	1·140	44·29	0·0007
29	17·9	1·1414	44·90	0·0007

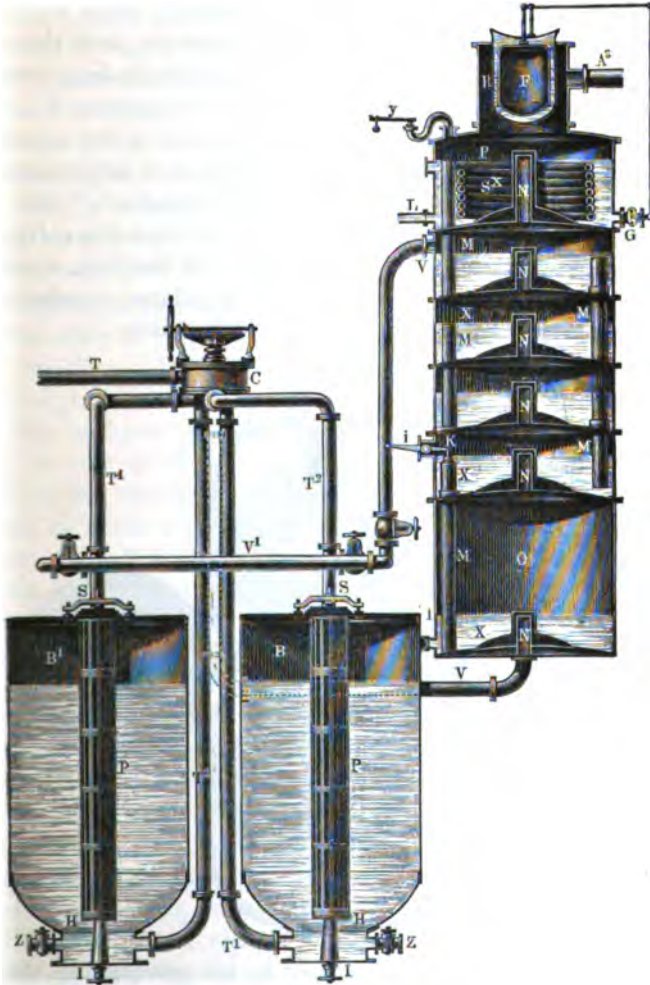
The result is attained more conveniently and quickly by the bromine-soda method, either by means of the azotometer or by the gas-volumeter (Vol. I. p. 185), connected with a "decomposing flask." Each c. c. nitrogen gas, reduced to  $0^{\circ}\text{C}$ ., 760 mill. pressure, and the dry state, corresponds to 0.001285 gram N, or 0.001561 gram  $\text{NH}_3$ , taking into account the so-called "absorption" of nitrogen; so that no reduction-tables need be applied here (comp. Lunge and Hurter's 'Alkali-maker's Handbook,' 2nd ed. p. 163).

In all cases the principle followed on treating these liquors is the same. They are first distilled *by themselves*, until all the ammonia present as carbonate (in gas-liquor also all sulphide) has been expelled, during which process it splits up into free  $\text{NH}_3$ ,  $\text{CO}_2$  (or  $\text{H}_2\text{S}$ ), and water. This operation is always performed in "distilling columns," or analogous apparatus, in which the newly arriving cold liquor causes the mixture of gases and steam to separate into liquid water and gases, so that ultimately a pretty pure and dry mixture of  $\text{CO}_2$  and  $\text{NH}_3$  is evolved, which is at once introduced into the apparatus for the preparation of ammoniacal brine (p. 25). The residue in the still contains the greater portion of the ammonia in the state of chloride, and is *boiled with lime* until the ammonia has been entirely expelled. The residue now remaining is a solution of calcium and sodium chloride, and is mostly run to waste; compare, however, the concluding portion of this chapter.

The apparatus which was used during a considerable time at the Solvay works for distilling the ammonia is described in the patent No. 1904 (1876), p. 6. It is founded mainly upon the well-known principle of spirit-rectifying apparatus; but it allows first the  $\text{NH}_3$ , already present as such or as carbonate, to escape before the quicklime is introduced, and it utilizes the heat generated in slaking the latter for distilling the ammonia; so that, besides this and the exhaust-steam of the engines, no special source of heat need be applied (comp. later on). Figs. 66 and 67 are a section and a plan of the apparatus. The liquor filtering from the bicarbonate first passes through the column A for distillation without lime, and then through the four stills B to B<sup>4</sup> for distilling with lime. The stills B, B<sup>1</sup>, B<sup>2</sup>, B<sup>3</sup> communicate with each other by a distributor C, similar to those used in gas-works, which permits any boiler to be isolated without interrupting the distillation in the others. As

a rule, one still is stopped for discharging and recharging while the other three are working. The exhaust-steam from the engines passes through the pipe T into the distributor C, and from this by

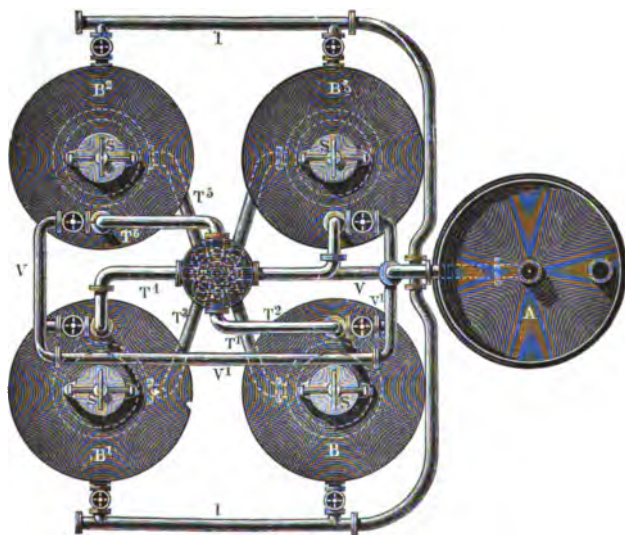
Fig. 66.



T<sup>a</sup> to the longest-working still B; from here it returns by T<sup>s</sup> into the distributor C, and passes through T<sup>s</sup> into the second still B<sup>1</sup>. Similarly it passes into the last-filled still B<sup>2</sup>; so that

fresh steam enters precisely that still in which the liquor has only to be freed from the last traces of  $\text{NH}_3$ . When the steam leaves the last still  $B^2$ , it again enters the distributor and passes through  $V$  into the distilling-column  $A$ , where it causes the expulsion of the ammonia present as such or as carbonate. In this column the mother liquor from the bicarbonate running down acts so that the steam is condensed, while the  $\text{NH}_3$  passes on, and the mother liquor receives a preliminary heating. The last cooling is effected in the upper part of the column by the refrigerator  $P$ , so that from the pipe  $A^3$  only gaseous ammonia with some ammonium carbonate escapes, but no steam—which is very important, since the gas from here passes direct into the “dissolvers” for brine, and this must not be diluted with water. Within the refrigerator  $P$  is the cooling-coil  $S$ , filled with liquid to be distilled, which thus receives a first heating. On the top is a regulator, consisting of a float  $F$  in a vessel  $R$ , and containing a little water.

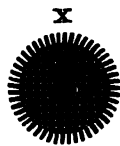
Fig. 67.



This water is more or less heated by the gas passing through; the warmer it is, the lower the float descends, and ultimately opens a cock  $G$ , which admits fresh liquor into the coil—in the same way as the admission of steam into the distilling-apparatus is regulated. From the coil the liquor runs out by  $L$  into the

interior of the distilling-column, and from this by *l* into the lower still which has just been emptied and freshly charged with lime. When just enough liquor has collected in the lower part O of the column A to fill one of the stills, which can be seen by means of a gauge-glass, the valve K is closed by the lever *i*, and a further descent of liquor into O prevented. Otherwise the liquor in the column always runs off by the overflow M, whilst the central pipes N convey the  $\text{NH}_3$  gas and the steam. The convex false bottoms X, separately drawn in fig. 68, serve for distributing the steam in the liquid; they are perforated with many conical holes and are nicked all round. *y* is a safety-valve at the end of a swan-neck pipe filled with water or petroleum, which prevents the  $\text{NH}_3$  from corroding the metal of the valve.

Fig. 68.



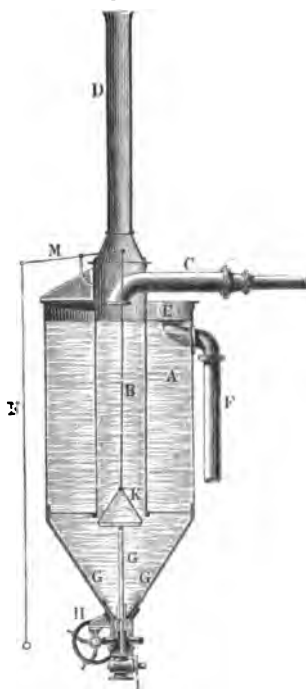
In the stills B to B' the ammonium chloride must be decomposed by lime. For this quicklime, straight from the kilns, is put through the doors S into the central (or lateral) cages P, which retain the unburnt pieces, stones, &c. The  $\text{NH}_4\text{Cl}$  liquor ascending in the still B slakes the lime; and the heat thereby evolved assists in the distillation: this can never take place with such violence as to cause any danger, since in this case the evolved gas and steam would force back the liquor and not permit it to enter into the cage. Thus the heat of the slaking lime and that of the exhaust-steam from T act at the same time.

Solvay in the same patent describes another apparatus for continuous distillation with a single column.

At the end of the distillation the exhausted liquor is run off by the cocks Z; and the bottom door I, which at the same time supports the bottom of the lime-cage P, is opened, so that the residue falls out of the latter. In order to separate the liquor, containing calcium and sodium chloride, from the suspended matter (if it is intended to be utilized), Solvay passes it through the self-acting decanting-apparatus, fig. 69. The hot liquor passes through the pipe C into a central pipe B, whence the steam escapes through the pipe D, while the liquor rises up in the vessel A and at the top runs over into the pipe F at E. The lime-mud settles at the bottom, is scraped off the same by scrapers moved by the hand-wheel H, and taken out at I. The conical valve K, moved by the lever M and the rod N, prevents the fresh liquor from disturbing

the settled lime-mud. The distillation is best carried on in a partial vacuum, produced by connecting the outlet T' of the dissolvers (fig. 3, on p. 26) with a water-piston pump; the gas, before reaching the pump, first passes through washing-apparatus for retaining any ammonia it may contain.

Fig. 69.



In a French patent, No. 130527, of 1879, Solvay mentions that he then separated the decomposition of ammonium chloride from the expulsion of the free  $\text{NH}_3$ , and that he effected the decomposition by calcium hydrate in the form of lumps produced by slaking quicklime with a solution of calcium or magnesium chloride.

The complicated apparatus shown in figs. 66 to 68 has been abandoned at the Solvay works in favour of the generally employed distilling-columns, consisting of two superposed parts, *e.g.* the shape described in Mond's patent, No. 715, 1883, shown in fig. 70. The upper narrower portion A serves for expelling the ammonium carbonate from the liquor running in at the top, as it



comes from the filters, by means of the steam coming from below. This upper part is generally made of cast-iron, the lower wider part, which serves for decomposing the  $\text{NH}_4\text{Cl}$ , of wrought-iron. The shape of the compartments of this lower part differs very much from that of the upper part, as the milk of lime, entering at *a*, must be able to gradually run downwards without stopping up the basins. Since all compartments must be frequently cleaned out, they are all provided with man-holes *b, b*. The spent liquor runs off at *c*; steam is also introduced here.

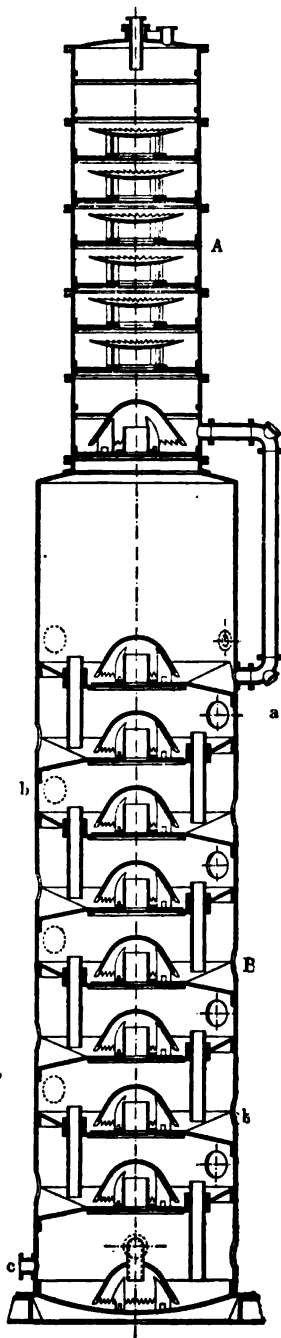
These columns are made of considerable size, up to 66 feet high and correspondingly wide. The milk of lime is generally introduced at two or three opposite places of the lower, wider portion; the lime-pump may be coupled with the liquor-pump in such manner that the quantity of lime always corresponds to that of the liquor sent through the column.

The German patent No. 28761 of the Soc. anon. des produits chimiques de l'Est, describes a terrace-shaped set of five pans with semicircular bottoms; the three upper pans serve for expelling the ammonium carbonate, the two lower ones, which are filled with inverted nicked-out lead spoons, for decomposing the ammonium chloride.

Another still of Solvay's (Engl. pat. 8169, 1889) is intended for removing  $\text{CO}_2$  and  $\text{H}_2\text{S}$  before the  $\text{NH}_3$ .

Hennebutte (Amer. pat. 253045), after expelling the ammonium carbonate, destroys the small quantity of this

Fig. 70.



remaining in the liquor with the ammonium chloride, as it causes troublesome frothing by the formation of calcium carbonate, by adding an acid to the liquor before putting in the lime. Wigg (Engl. pat. 10295, 1887), on the contrary, adds some calcium chloride to the alkaline liquor and removes the calcium carbonate formed by filtration.

The large quantity of lime required for decomposing the ammonium chloride makes the work with ammonia-stills for mother liquor much more troublesome than that with ordinary gas-liquor, containing much less fixed ammonia. Some of the column-apparatus mentioned have overcome this difficulty; but at some factories they still prefer the intermittent work in simple cylindrical stills with conical bottoms as described below, in which the process generally takes 12 hours. Such a still is described in Honigmann's German patent, No. 13782. ☐

Some ammonia columns are provided with agitating-gear for preventing an obstruction by the lime, *e. g.* P. Mallet's, shown in my 'Coal-tar and Ammonia,' 2nd ed. pp. 653 & 656; these are said to answer very well.

Fassbender (Zschr. f. angew. Chem. 1893, p. 167) describes the ammonia-stills as follows, in connection with the absorbers for ammoniacal brine. They consist of 4 or 5 boilers A, figs. 71 & 72, the distributor B, the distilling-column C, the cooler D, the ammonia absorber E, the vacuum-pump F, and the mother-liquor basin G.

The boilers A, with a conical bottom, serve for distilling the liquor with lime. Fig. 73 shows such a boiler with its fittings and pipes. Each boiler has two pipes connecting it with the distributor B, pipe *n* for the inlet and pipe *o* for the outlet of the gas. The latter ends at the top of the boiler, the former (*n*) passes through the same downwards and ends 4 inches above the lowest part of the bottom. About 18 inches above its end there is a sieve 5 feet in diameter. Before entering into the boiler, a branch-pipe *p* connects pipes *n* with the blow-off pipe *r* for spent liquor: *p* can be shut off by the bell-valve *x*. The shut-off cock *r* of the blow-off pipe is placed behind the junction with *p*. The blow-off pipe dips into the boiler almost as deeply as the steam-pipe; therefore during the distillation, when *x* is open, steam blows through *p* and *r* into the boiler and keeps the blow-off pipe clean. The prevention of escape from the blow-off cock of liquor and steam is secured by a stop-flange behind the cock. The waste liquor is carried away by

a pipe not shown in the diagram, and serves for a preliminary heating of the boiler-feed water before leaving the works.

Fig. 71.

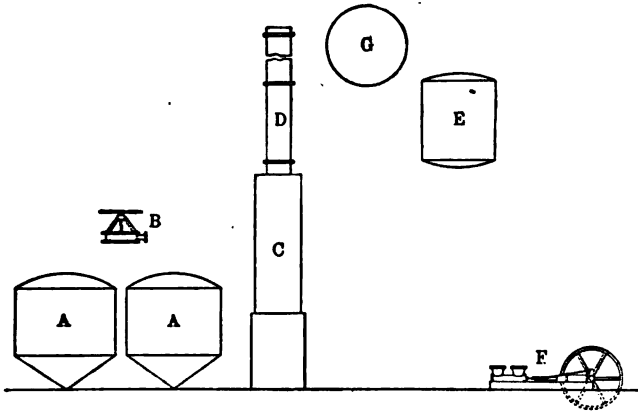


Fig. 72.

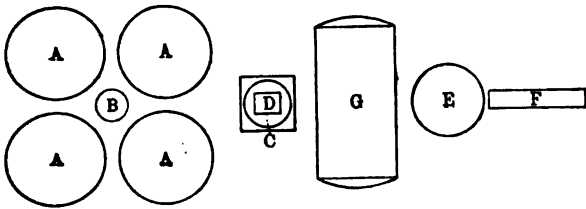
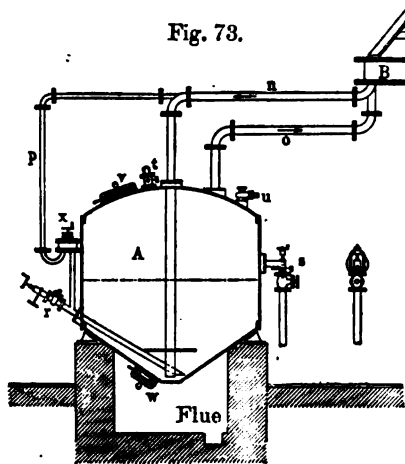


Fig. 73.



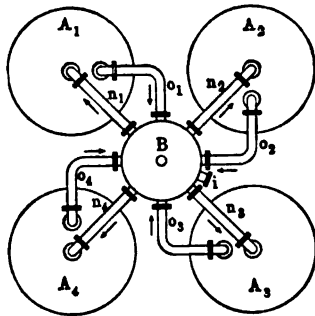
The boilers have a valve *s* for feeding with mother liquor, between which and the boiler a stop-flange is arranged. This is necessary for the following reason :—The 4 or 5 boilers of a set are fed from a main-pipe. As in the boilers during distillation the pressure is greater than in the mother-liquor pipe, in the case of the valve leaking steam would enter into the main-pipe and disturb the charging of the boilers put out of turn, unless this was prevented by the stop-flange, which is shown in side-view as well.

The steam-space of these boilers is connected with that of the column, in order to equalize the pressure during the charging with mother liquor. This pipe can be shut off by a valve *t*, which it is best also to provide with a stop-flange. Tap *u* serves for introducing the milk of lime. This is run into the boiler to be charged by a short piece of india-rubber tube, strengthened by a wire spiral, which serves for all the boilers. After charging, this tube is removed, and the inlet is shut by a screw-cap. On the cover of the boiler there is a man-hole *v*, 16 inches wide, in the bottom part a cleaning-hole *w*, 10 inches wide. There is also a pressure-gauge and several small taps for taking samples and for gauging the heights of the liquor. The boiler is supported on brickwork by means of 8 brackets, riveted to the conical parts in such manner that its bottom is easily accessible.

The distributor B serves for cutting off one of the boilers from the steam-pipes, and for feeding the others in rotation with steam. Fig. 74 shows how the distributor acts in a set of 4 boilers. *A*<sub>2</sub> is cut off, in order to be charged with mother liquor and lime. The steam enters through *i* into the distributor, and passes through *n*<sub>3</sub> first into *A*<sub>3</sub>, which is nearly finished. From *A*<sub>3</sub> the steam goes through *o*<sub>3</sub> into the distributor and then through *n*<sub>4</sub> into *A*<sub>4</sub>. From *A*<sub>4</sub> it gets back into the distributor and through *n*<sub>1</sub> into *A*<sub>1</sub>, which is the boiler last put into series, and containing the strongest mother liquor.

From *A*<sub>1</sub> the steam, now charged with ammonia, goes for the last time into the distributor and then passes over to the distilling-column. When *A*<sub>2</sub> has been charged, *A*<sub>3</sub> will be finished, and

Fig. 74.



its liquor can be blown off. By moving the distributor fresh steam is first introduced into boiler A (fig. 73), passes through  $A_1$  and  $A_2$ , and at last into the column.  $A_3$  is now cut off and ready for charging.

Fig. 75.

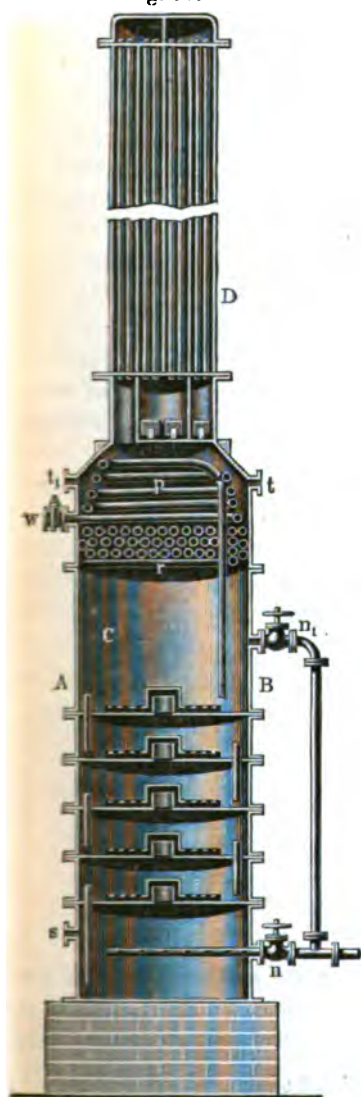


Fig. 76.



These changes were at first produced by valves, but these had two drawbacks. There was a loss of pressure, which does not signify with steam direct from the steam-boilers, but is quite sensible when working with exhaust steam and in a vacuum. Moreover, the valves did not wear well; the spindle exposed to the atmosphere of ammoniacal vapour was quickly corroded, and all face-joints required to be kept tight were also very much acted upon, so that all joints had to be made with india-rubber, which had to be frequently renewed. This is avoided by the described distributor, on the same principle as that applied by Solvay, p. 108, both of these being copied from Clegg's coal-gas distributor.

The distilling-column employed by Fassbender for boiling off the ammonium bicarbonate is shown in figs. 75 and 76. The

lower portion exhibits the universally known construction, and requires no further explanation. There are 6 compartments for driving off the bicarbonate. To the lowest of these is attached the waste-liquor pipe *s* and the gas-inlet *n*. The top compartment is provided with necks *w*, *t*, and *t*<sub>1</sub>. *t* effects the equalization of pressure between the column and that boiler which is being charged with liquor through *s*; *t*<sub>1</sub> effects the same purpose between the column and the mother-liquor reservoir. This compartment also contains a coil *p* for heating up the mother liquor. Below this coil there is a number of stoneware balls *r*, over which runs the liquor condensed in the coil and the cooler, and is thereby deprived of its ammonia by the ascending vapours. Through *w* the mother liquor enters into the coil.

The cooler D forms a continuation of the distilling-column. It is a tubular cooler of any desired shape. Fassbender, *loc. cit.*, describes two forms of it, which he proposes as improvements upon the simple form shown here; but the most varied forms of columns and coolers, as they are found in the distillation of spirit of wine, of benzol, &c., can be employed here, always supposing their size to be suitable for the purpose in hand\*.

If the distilling-apparatus is properly constructed and carefully worked, sometimes the ammonia gas is obtained in such a state of dryness that the ammoniacal brine need not be enriched later on by adding solid salt to it (comp. p. 56).

Fassbender (*loc. cit.* p. 226) gives detailed calculations for the dimensions of apparatus to be employed for a certain amount of work; but I refrain from entering upon them, as they seem to refer only to the special construction of apparatus he has in view.

Fig. 77.

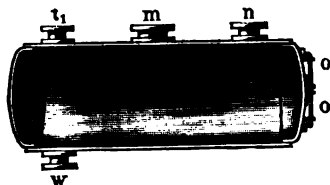


Fig. 78.



Fassbender also describes a *reservoir for mother liquor* of the shape sketched figs. 77 and 78. It is a closed cylinder, placed at some distance above the ground, the mother liquor from the filters

\*. Comp. my 'Coal-Tar and Ammonia,' 2nd edition, p. 462 *et seq.*

being forced into it by compressed lime-kiln gas. The neck  $n$  serves for introducing the mother liquor.  $t_1$  communicates with the neck  $t_1$  in fig. 75 by means of a pipe, so that the pressure in both apparatus is always the same, and the reservoir follows the variations of pressure in the still. The outlet  $w$  is connected by a pipe with the branch  $w$  of the coil of the distilling-column, fig. 75, a tap with stuffing-box being interposed;  $m$  is a man-hole and  $o$  gauge-cocks. The bottom of this reservoir is at least 13 feet above the inlet  $w$  of the column. As the diameter of the reservoir is about 8 feet, any variations of the depth of liquor within cause only a slight difference in the average rate of supply of liquor for the column, which is of great advantage for regular work.

*Quantity of Lime used in the Ammonia-Stills.*—The work to be performed in the ammonia-stills is calculated by Fassbender on the basis of the data given on p. 70 *et seq.*, in the following way:—For a daily production of 10 tons soda-ash we find the subjoined quantities of  $\text{NH}_3$  in the mother liquor:—

$\text{NH}_3$ as sulphate .....	61.36 kilog.
„ bicarbonate .....	690.30 „
„ chloride .....	3466.84 „
	<hr/>
	4218.50 „

This quantity must be distilled daily from 81 cub. metres of mother liquor; this means hourly  $\frac{4218.5}{24} = 175.77$  kil.  $\text{NH}_3$ .

In order to calculate the requisite quantity of lime, he assumes that four-fifths of the ammonium bicarbonate is boiled out in the column, and one-fifth, in the state of monocarbonate, gets into the boiler-still. The waste liquor contains 25 kil.  $\text{NH}_3$ , which must be deducted. In order to completely decompose the  $\text{NH}_4\text{Cl}$ , we must employ an excess of lime, say 25 per cent. We have therefore to deal with:—

$\text{NH}_3$ as sulphate .....	61.36 kilog.
„ carbonate $\frac{690.3}{5}$ .....	138.06 „
„ chloride .....	3466.84 „
Loss in distilling, &c. ....	25.74 „
	<hr/>
	3692.00 „

This requires  $\frac{3692 \times 28}{17} = 6081$  kil.  $\text{CaO}$  in theory, or, adding

the excess of 25 per cent., 7600 kil. CaO; or making some allowance for loss as dust, &c., 8085 kil. 94-per-cent. quicklime. This quantity is made up to 30 cub. metres (=1060 cub. feet) milk of lime; in this case the milk has still sufficient fluidity.

The milk of lime, hot from the operation of slaking, is brought up nearly to the boiling-point by the exhaust-steam from the stone-hoist and the direct steam of an injector serving as an agitator. It arrives at its destination at about 90° C. As it is diluted by the water condensing from the injected steam, we must calculate upon 33 cubic metres per day or 1375 litres per day.

*The testing of the lime* is performed as described on p. 45. *Milk of lime* can be tested in exactly the same way, but the stock must be well mixed up before taking out a sample, and this must be well shaken up before each test. The requisite quantity is then quickly taken out by a pipette, which is washed outside, before running its contents into the beaker in which the titration is made. The lime adhering to the inside of the pipette is removed by rinsing it with water, or if necessary with some of the standard acid.

The subjoined table (reduced from that given by Blattner, Dingl. Journ. ccl. p. 464) gives the quantity of CaO per litre of a milk of lime according to its specific gravity, taken at 15° in the following manner:—In the case of thin milk the reading must be quickly taken. For thick milk the cylinder employed must be pretty wide, the hydrometer should be put lightly in, and the cylinder slowly turned round on the table, so that it undergoes a slight shaking, until the hydrometer ceases to descend.

Degrees Twaddell.	Grms. CaO per litre.	Lb. CaO per cubic foot.	Degrees Twaddell.	Grms. CaO per litre.	Lb. CaO per cubic foot.
2	11.7	0.7	28	177	11.1
4	24.4	1.5	30	190	11.9
6	37.1	2.3	32	203	12.7
8	49.8	3.1	34	216	13.5
10	62.5	3.9	36	229	14.3
12	75.2	4.7	38	242	15.1
14	87.9	5.5	40	255	15.9
16	100	6.3	42	268	16.7
18	113	7.1	44	281	17.6
20	126	7.9	46	294	18.4
22	138	8.7	48	307	19.2
24	152	9.5	50	321	20.0
26	164	10.3			



*Heating the Ammonia-Stills.*—This was formerly always done by the exhaust-steam of the blowing-engine which takes away the lime-kiln gas. Solvay's patents mention this several times, and I have frequently seen it done in practice. Pick, in his book 'Die Alkalien,' 2nd ed. p. 105, says distinctly—"The distillation is probably without exception performed by exhaust-steam." This is, however, decidedly a mistake. Fassbender (Zsch. f. angew. Chem. 1893, p. 139) speaks of employing either boiler-steam or exhaust-steam. At the close of his paper (p. 264) he certainly states that the latter is preferable, but he does not substantiate this for the case where the blowing-engine is worked with condensation (comp. next page). Schreib (Chem. Zeit. 1890, p. 493), in direct contradiction to Pick, says: "Probably direct (boiler-)steam is mostly used for boiling." I have found this to be the case at some of the best works I have visited (comp. also *infra*).

According to Fassbender's detailed calculations (*loc. cit.* p. 224), the production of 10 tons ammonia-soda, in which 4218·5 kil.  $\text{NH}_3$  has to be liberated, theoretically requires in winter 1464, in summer 1348 kil. steam of 1·5 atm. absolute tension per hour. Practically he was able, with the plant described by him, working with exhaust-steam and a vacuum, to expel for 1 kil. steam (in spring) 2·2 kil.  $\text{NH}_3$ ; hence he would use in winter 1976, in summer 1860 kil. steam per hour. The difference between this quantity of steam for the stills and that calculated above for heating-up, &c., yields the quantity of steam to be dealt with by the cooler. This is 512 kil., of which the greater portion, say 345 litres of water, flows back into the still; about 66·6 litres per hour is carried away into the ammonia-absorber. The quantity of liquid daily removed by distillation is therefore:—

	In winter.	In summer.
from the mother liquor.....	81	81 cub. metres.
„ milk of lime .....	33	33 „
„ steam used for heating.	43·4	40·6 „
	<hr/> 157·4	<hr/> 154·6

This steam, of 1·5 atm. absolute<sup>1</sup> pressure, Fassbender takes from the exhaust of the blowing-engine, calculated on p. 49. He also calculates the following data for the *vacuum-pump* belonging to the ammonia-stills, for 10 tons soda-ash per day:—

Pressure of steam 6 atm. on entering, 1.63 atm. on leaving the cylinder; cut-off at one third; stroke 27.5 inches; 42.8 strokes per minute; diameter of steam-cylinder 10.8 inches; diameter of pump-cylinder 19.2 inches; indicated H.P. 18; quantity of steam passed through the inlet-valve 1.20 lbs. per hour.

When speaking of the application of exhaust-steam, "practical men" frequently, although not consciously, make the totally erroneous assumption that this kind of heating costs nothing. Even in such cases where otherwise the exhaust-steam of a high-pressure engine would freely puff out into the air, as it is certainly found to take place in most cases at chemical works, the utilization of the exhaust must cause a certain counter-pressure on the piston, even by the friction in the pipes, and this must lessen the work done, or cause an excess consumption of coals for the engine. Still in this case that extra coal is more than counterbalanced by the saving effected by utilizing the exhaust-steam for heating-purposes. Where, therefore, it is not worth while working a condensing steam-engine, that utilization is quite rational. This holds good, for instance, of the small engines employed for fan-blasts, liquor-pumps, &c.

A totally different result is obtained in such cases where large engine-power is required, *e. g.* for blowing-engines connected with Solvay towers. Here the only rational proceeding is to employ compound engines, with expansion and condensation, thus utilizing the energy of the steam as much as possible for the engine itself; for the stills fresh boiler-steam is used. At very large works, where there are whole nests of steam-boilers, preferably fired by means of mechanical stokers, the steam-pressure can be kept very uniform, and this is a great advantage when heating the ammonia-stills with boiler-steam, as this uniform tension causes the evolution of ammonia, and consequently the whole manufacturing process, to be equally uniform and steady.

*Cooling the Vapours from the Ammonia-Stills.*—These vapours contain, besides  $\text{NH}_3$  and  $\text{CO}_2$ , a good deal of steam, and are neither cold nor dry enough for direct use in the apparatus where the brine is saturated with ammonia. They are therefore always cooled down before entering into that process. We have alluded on pp. 108 and 116 to apparatus serving for this purpose. The liquid condensing in the cooling-apparatus can be used in various ways, as mentioned on p. 98.

*The loss of ammonia* is, of course, one of the most important factors in this manufacture. In the first period after the discovery of the ammonia-soda process it sometimes amounted to 20 parts of ammonium sulphate for 100 of soda-ash; we cannot be surprised that under these circumstances no competition with the Leblanc process was possible. The first apparatus realizing a sufficient economy of ammonia was Solvay's; then followed Honigmann's, and later on several others. Even in 1878 I was told at Northwich that the loss of ammonium sulphate amounted to 8 per cent. of the soda-ash, but that at Varangéville, with the same kind of plant, it was only 4 per cent. Down to 1890 that amount, or at most 3 per cent., seems to have been considered a minimum, below which it was not possible to go in the long run. But the sharp decline of prices has necessitated the employment of increasingly efficient washing arrangements, of stronger carbonic acid, and of other improvements, so that manufacturers assert that nowadays the loss of ammonium sulphate must not exceed 1 per cent. to any considerable extent, to enable them to compete with others.

One of the means of diminishing the loss of ammonia is to work the ammonia-stills under diminished pressure (pp. 31 and 112), by employing behind the apparatus for manufacturing the ammoniacal brine an air-pump, which draws the gases through this apparatus and the washers connected therewith, and therefore produces an aspirating action further back in the ammonia-stills. This effects a considerable saving of ammonia.

#### *Treatment of the Waste Liquor.*

The residual liquor from the ammonia-stills is essentially a solution of calcium and sodium chloride, holding in suspension a considerable quantity of solid substances, especially lime.

This liquor must at all events be *clarified* before being allowed to run into a public water-course. Solvay describes a continuously acting decanter attached to the ammonia-stills, which has been shown in fig. 69, p. 109. But of course any other apparatus for filtering or filter-pressing may be employed for this purpose; or else some kind of settling-tanks or the like must be provided, unless the works happen to be situated on a large lake whose water is not sensibly polluted by the inflowing mud. The public authorities everywhere require this mud to be kept out of the public

watercourses. Usually large pits are provided near the works, in which the lime-mud is deposited; the clear liquor is allowed to soak into the ground if this is sufficiently porous, but if not it is drawn off at the top and run into some stream or canal. Undeniably these mud-pits and the liquor draining from them constitute a rather troublesome feature in the ammonia-soda manufacture, but this cannot for a moment be compared with the nuisance caused by the tank-waste heaps from Leblanc works (Vol. II. p. 820).

*The mud settling from the waste liquor*, if it contains enough caustic lime, is sometimes used for a second operation in the columns. It has also been attempted to employ it for the manufacture of Portland cement, for which it ought to be very well adapted (Vol. II. p. 879). A new patent by Rigby, Ditton, Neill, and Carr (No. 19705, 1893) refers to this matter.

The clear liquor ultimately left usually contains about 150 grams of salts per litre, viz. about equal parts of calcium chloride and sodium chloride, with slight traces of ammonia. It has been frequently proposed to recover from it the sodium chloride by evaporation and fishing, but this hardly pays for itself; at least in nearly every case I know of the whole of this liquor runs to waste, and thus carries away all the chlorine equivalent to the soda manufactured in the shape of calcium chloride, apart from the excess of sodium chloride.

*The chemical examination of the final liquor* must extend to the excess of lime and free ammonia. Both are best found by boiling 100 c. c. till the whole of the  $\text{NH}_3$  has been given off; this is condensed in normal hydrochloric acid and titrated. By diluting the boiled residue to 100 c. c., cooling down, filtering, and applying the Nessler test to the filtrate, it is seen whether the expulsion of the  $\text{NH}_3$  has been perfect. The lime is estimated by adding to 50 c. c. of the muddy liquor, which is thoroughly shaken up before taking out the sample, an excess of ammonium sulphate, boiling again and receiving the  $\text{NH}_3$  escaping, which corresponds to the excess of lime, in standard acid. This indicates both caustic lime and calcium carbonate; if these two are to be separated, the caustic lime is separately estimated by oxalic acid and phenolphthaleine, as explained on p. 45.

Jurisch ('Verunreinigung der Gewässer,' p. 23) makes the following statements regarding the waste liquor of ammonia-soda works.

On distilling with a steam-coil (system Mallet-Boulouvard) the manufacture of a metrical ton of soda-ash produces 7367 litres of waste liquor, composed as follows: spec. gravity 1.142; per litre 70 grm. NaCl, 160 grm. CaCl<sub>2</sub>, 27 grm. CaO (as hydrate and carbonate), 0.05 grm. NH<sub>3</sub>. On distilling with open steam (as in all other systems) the quantity of waste liquor per ton of soda-ash is 11 cubic metres of spec. gravity 1.037 to 1.125, averaging 1.091. During the years 1882 and 1883, at La Madeleine, near Lille, Jurisch found the composition of the waste liquor to be:—

	Minimum.	Maximum.	Average.
Specific gravity .....	1.067	1.100	1.087
NaCl grams per litre ...	55	135	80
CaCl <sub>2</sub> „ „ „ ...	15	50	25
H <sub>2</sub> CaO <sub>2</sub> „ „ „ ...	17	32	25
CaCO <sub>3</sub> „ „ „ ...	2	40	5
NH <sub>3</sub> „ „ „ ...	0	0	0

Schreib (Chem. Zeit. 1892, p. 693) points out that, according to Jurisch's analyses, the yearly average at the Madeleine showed the enormous consumption of 400 salt to 100 soda-ash, and a loss of 75 quicklime, apart from 25 CaCO<sub>3</sub>; also that instead of 1.5 cub. metr. more than 4 cub. metr. of liquor had been produced, and a correspondingly large amount of fuel must have been consumed in the ammonia-stills. [The conclusion to be drawn from this is that either Jurisch's figures refer to a very small and faulty experimental plant, or else that his samples were accidentally very inferior, and indicate anything but the *average* composition of the liquor. At all events these analyses of Jurisch's are not of the slightest value for judging the practical conditions of the case, no more than others showing an excessively *small* consumption of salt.]

At some works visited by me, I was told that the final liquor was brought down to 0.01 grm. NH<sub>3</sub> per cubic metre; but they did not go so far as to put the loss of ammonia = *nil*, as Jurisch does for the La Madeleine works, and that all the year round! No factory whatever has ever attained to such perfection.

Schreib (Chem. Zeit. 1894, p. 1793) mentions a simply monstrous "Expert's Report," advising refusal of leave to erect ammonia-soda works. According to that Report, trees had been killed by the calcium-chloride liquor at a distance of two

kilometres (about  $1\frac{1}{2}$  mile) from the mud-settlers; rye, fruit-trees, &c. had also been killed by the alkali-dust from the works at the same distance. If such were the case, the great majority of chemical works would be surrounded by a desert!

*Proposals for Utilizing the Calcium Chloride contained in the Waste Liquor.*

We shall not in this place treat of those proposals which aim at obtaining *chlorine* (or  $\text{HCl}$ ) from the  $\text{CaCl}_2$ ; this will be done in a special chapter of Book III. We will here only refer to proposals in another direction.

Thovald Schmidt (Chem. News, xxxiv. p. 201, xxxvii. p. 56) adds to the concentrated solution of  $\text{NaCl}$  and  $\text{CaCl}_2$ , obtained in recovering the  $\text{NH}_3$ , a concentrated solution of kelp. The potassium, sodium, and magnesium sulphates in the latter are thereby decomposed, and  $\text{CaSO}_4$  and  $\text{Mg}(\text{OH})_2$  precipitated in a form suitable for use as "pearl hardening" in paper-making (comp. Vol. II. p. 721). The last traces of the sulphates are removed by barium chloride. To the clear solution lead nitrate is added till all the iodine has been precipitated as  $\text{PbI}_2$ , which is filtered off and worked up for iodine. The filtrate is heated, lime and magnesia precipitated by soda, the  $\text{KCl}$  converted into  $\text{KNO}_3$  by  $\text{NaNO}_3$ , and the saltpetre removed by crystallization. There remains a solution of  $\text{NaCl}$  with traces of  $\text{KCl}$  and of  $\text{NH}_3$  (from the last operation): this is again submitted to the ordinary ammoniacal soda-process. This process can only pay in very exceptional circumstances, where salt is very dear; but then the ammonia process would be out of place. Later on (Chem. News, xxxviii. p. 203) Schmidt gave a rather detailed description (but without diagrams) of the apparatus used in the ammoniacal soda-manufacture at Aalborg (now stopped). According to his statements, there are needed daily for 10 tons of soda:—salt, 16 to 17 tons; coal, 17 to 18 tons; coke, 3 tons; limestone, 12 tons; sulphuric acid of  $106^\circ \text{Tw.}$ , 2 cwt.; ammonia salt, from 4 to 6 cwt.; and 45 men.

A recent detailed description in the Chem. Zeit. 1891, p. 821, which is written to draw attention to this process, proves that it had undergone no change, and probably had not been in actual use, for some years. The process is adapted only to local circumstances,

where there is a large accumulation of kelp, and in this case it may be advantageously used.

Richardson (Engl. pat. 10418, 1884) proposes to make pearl-hardening from the  $\text{CaCl}_2$  liquor by adding to it ammonium sulphate; the ammonium chloride formed is to be recovered by evaporation and crystallization. [But, apart from the many faults of this process, would there be a ready sale for the pearl-hardening?]

Webster (Engl. pat. 12344, 1885) forms a paste of calcium-chloride liquor and slaked lime or calcium carbonate; this is evaporated, dried, fused, cast in moulds, and used as a flux in metallurgical operations.

Schreib (Chem. News, 1890, lxiv. p. 4) describes a local utilization of calcium chloride liquor at a small factory producing 1000 tons of ammonia-soda per annum. This liquor is decomposed by sulphuric acid or sulphates, to obtain pearl-hardening for use at paper-works or for painting cardboard (comp. *supra*). Actually sulphuric acid or nitre-cake was employed, and the dilute hydrochloric acid formed in this process was also utilized. Thus 30 tons of pearl-hardening per week was manufactured. Schreib proposes to do the same thing in other places with ordinary salt-cake, and to re-introduce the resulting solution of sodium chloride into the ammonia-soda manufacture. [It is extremely doubtful whether a sufficiently large sale could be found for such enormous quantities of pearl-hardening, although this article can be employed in many cases, such as china-clay, and is much superior for paper-making to ground plaster of Paris, on account of its fibrous crystallization.]

*Other Processes for treating the Ammonium-Chloride Liquors filtered from the Bicarbonate.*

Schreib (Germ. pat. 36093; Zsch. f. angew. Ch. 1889, pp. 445, 486) subjects the liquor filtered from the bicarbonate to artificial cooling, at least down to  $10^\circ$ , better to  $5^\circ \text{C.}$ , adds solid sodium chloride and passes ammonia and carbonic acid into it. A great portion of the ammonium chloride crystallizes out; the mother liquor goes back into the process and is again passed through the carbonating apparatus. The ammonium chloride is either distilled with lime in the usual way, or else it is mixed in the dry state with calcium carbonate or the mud from causticizing soda, in.

order to convert it by heating into ammonium carbonate. In the former case the advantage consists in the high concentration of the solution, and the residue left on distillation being an almost pure concentrated solution of  $\text{CaCl}_2$ . The latter case is even more profitable, since the products are ammonium carbonate and a residue of fused calcium chloride, which is far more suitable for the manufacture of chlorine or hydrochloric acid than the ordinary waste  $\text{CaCl}_2$  liquor from the ammonia-stills. This process effects a saving of at least 80 parts salt for 100 soda-ash manufactured. In spite of these theoretical advantages, Schreib's process has found no practical application. Probably the difficulty of cooling such large quantities of liquids and a greater loss of ammonia are against it. Klingbiel (*Chem. Zeit.* 1886, p. 1335) criticizes it very adversely; he asserts that no ammonium chloride at all is separated, but he seems to have neglected the cooling required by Schreib.

Young (*Engl. pat.* 2988, 1872) prescribes decomposing the  $\text{NH}_4\text{Cl}$  solution by  $1\frac{1}{2}$  equivalents of calcium or magnesium carbonate. He could not, however, in spite of prolonged boiling, drive the decomposition further than two-thirds, and had to finish it with caustic lime.

Teed (*Journ. Soc. Chem. Ind.* 1885, p. 709) proposed running the  $\text{NH}_4\text{Cl}$  liquor first down a tower filled with lumps of limestone, whereby much of the ammonia is expelled as carbonate. His experiments were made on a small scale, with an apparatus 5 feet 4 inches high. He believes that his arrangement is much superior to Young's process.

Schreib (*Zsch. f. angew. Ch.* 1889, p. 211) made a number of experiments on the decomposition of ammonium chloride by calcium carbonate in an aqueous solution. The rate of decomposition is greatly influenced by the degree of fineness of the calcium carbonate and by the concentration of the solution. With an excess of  $\text{NH}_4\text{Cl}$  the decomposition took twice as much time with finely ground limestone than with freshly precipitated calcium carbonate, three times as much with finely ground marble, and very much longer with limestone in pieces. Still more difficult is the task actually presented in practical work, viz., complete decomposition of the ammonium chloride by an excess of calcium carbonate. At first the reaction proceeds quickly, then slowly, and it takes considerable time for completion. (It seems preferable to arrest the process at an advanced stage, and



to complete the decomposition by caustic lime.) Limestone is altogether excluded, for it would cost more to grind it to the sufficient degree of fineness than to burn it into quicklime. But the mud from causticizing soda (Vol. II. p. 753) might be utilized: this has practically no value; it is in a state of fine division, and might be pumped at once into the still after being stirred up with water into a "slurry." Its constant percentage of caustic soda would be really an advantage. This material (which, of course, can only be obtained at factories where caustic soda is made) is not easily worked in continuously running column-apparatus, but very well in plain, intermittently run cylinders with conical bottoms, with direct steam blown in at the deepest part, which keeps the mud in constant motion and prevents it from settling at the bottom.

The decomposition of ammonium chloride by calcium carbonate forms also the subject of a German patent (No. 14186) by the Soc. an. des prod. chim. du Sud-Ouest. The solution of  $\text{NH}_4\text{Cl}$  remaining after driving off the ammonium carbonate is evaporated in iron vessels coated with lead, till the ammonium chloride has been separated in a solid form. It is then heated with powdered limestone or dolomite in narrow cast-iron retorts. The vapours are condensed in special coolers with addition of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in such a way that solid ammonium bicarbonate is formed. [Lead-coated iron vessels will not stand the action of a solution of ammonium chloride for any length of time.]

Wigg and Pratt (Engl. pat. 3673, 1884) again patent the decomposition of solid ammonium chloride with calcium carbonate. The  $\text{CaCl}_2$  remaining behind is to be decomposed by sulphuric acid into  $\text{HCl}$  and  $\text{CaSO}_4$ .

Solvay (Germ. pat. 16229) treats the ammonium-chloride liquor, instead of quicklime, with *natural basic phosphates*. These are ground, freed from the lighter calcium carbonate by levigation, and burned, or else used in the unburnt state. If used in the burnt state, the free lime mixed with the phosphate produces free  $\text{NH}_3$ ; if used unburnt, ammonium carbonate is liberated. In both cases purified calcium phosphate remains behind and is washed with water. As it is not possible in this case to bring about the complete decomposition of the  $\text{NH}_4\text{Cl}$  by an excess of  $\text{CaO}$ , which would leave the phosphate too impure, a special methodical treatment must be adopted. [This process cannot, of

course, receive any but a very restricted application in special cases.]

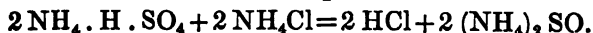
Jarmay (Engl. pat. 10419, 1886) causes the ammonium chloride to crystallize by artificial cooling, adds NaCl, cools again in order to separate more  $\text{NH}_4\text{Cl}$ , and repeats this several times. The last mother liquor is returned into the ammonia-soda process instead of brine, and thus the NaCl otherwise wasted with the final liquor is utilized, while the distillation for ammonia is saved. [What is to be done with all the ammonium chloride?]

*Transformation of Ammonium Chloride into Ammonium Sulphate.*

Mond (Engl. pat. 3820, 1883) proposes to distill the mother liquor filtered from the bicarbonate till all ammonium carbonate has been expelled, and to continue the evaporation in open vessels, fishing out the NaCl as it separates, till only dry ammonium chloride remains. This is heated with an excess of sulphuric acid till all HCl has been driven off, and acid sulphate,  $\text{NH}_4\text{H}\cdot\text{SO}_4$ , is left behind, which is either converted into ordinary sulphate of ammonia by addition of free ammonia, or employed for the manufacture of superphosphates. [It is hardly necessary to say that this process could never be applied to more than a very small portion of the ammonia-soda manufacture.]

Gilloteaux (Germ. pat. 49503) proposes the following reactions:—

1. Ammonium chloride is heated with acid sodium sulphate, or, preferably, ammonium sulphate, thus expelling HCl and leaving neutral sodium and ammonium sulphate behind:



2. The ammonium sulphate is heated, as in Carey and Hurter's process (comp. Chapter VIII.), in a current of steam, thus liberating half of the ammonia and forming acid ammonium sulphate, which is again utilized in the first reaction.

*Decomposition of Ammonium Chloride by Phosphoric Acid.*

O. N. Witt (Germ. pat. 37395) decomposes ammonium chloride by phosphoric acid; HCl is driven off and ammonium phosphate is left behind, which on heating to a higher temperature gives off the ammonia; glacial phosphoric acid remains and is used over again.

Jurisch (Dingl. Journ. cclxvii. p. 424) has examined this process in the laboratory. He finds that by means of a great excess of phosphoric acid, 99 per cent. of the HCl can be driven off at 300°. The residue consists of 4 mol. free phosphoric acid, 4 mol. ammonium phosphate, and 2 mol. ammonium pyrophosphate. On heating this to 400°, 63.6 per cent. of the NH<sub>3</sub> escapes as such. By using the residue over again, 86 per cent. of the NH<sub>3</sub> can eventually be recovered. But in doing this even silver and platinum vessels are strongly acted upon; no other material resists the fusing phosphoric acid, and consequently there is no technical possibility of carrying out Witt's process [which has never been done].

The processes in which the ammonium chloride is decomposed by *magnesia* instead of lime, in order to produce hydrochloric acid or chlorine from the magnesium chloride formed, as well as those in which dry ammonium chloride is *vaporized* and the mixture of ammonia vapour and chlorine separated into these two substances, will be treated in the section "Chlorine."

We shall then see that all processes aiming at separating the ammonium chloride from the mother liquors in a solid form are attended with considerable difficulties.

#### COMBINATION OF THE VARIOUS APPARATUS FOR THE AMMONIA-SODA MANUFACTURE.

We have already in several places briefly mentioned combinations of all the apparatus for this manufacture as proposed by various inventors, *e. g.* by Fassbender (p. 112). We shall here describe such a combination as it is employed at the large Solvay works, and as it may also be used for other methods, with the necessary modifications.

We begin with the *lime-kiln* (p. 36), to which belongs a mechanical hoist for limestone and coke, and a tramway for taking away the lime. The latter is carried in iron waggons, and is tipped into a *vessel for slaking the lime*, from which the milk of lime flows into a reservoir, placed again at a lower level, in order to be pumped into the ammonia-stills as required.

From the top of the lime-kiln the gas passes through one or two *washers* (p. 45), where it is purified from dust and sulphurous acid, and is cooled, and then into the *blowing-engine* (p. 48). If

the pumping-engine is a condensing-engine, there is no exhaust-steam to dispose of. In the contrary case the exhaust-steam from the blowing-engine, the vacuum-pump, &c. serves for heating the ammonia-stills. The gas discharged from the blowing-engine, which has become reheated under compression, passes again through a cooler (usually worked by injection of water) and then into the carbonator, with branches for raising liquids, &c. The purer carbonic-acid gas from the bicarbonate calciners is, for simplicity, frequently mixed at once with the lime-kiln gas.

On the other hand, the *brine* (purified from earthy salts) is first employed in the various *washers* (pp. 25 and 33) for treating all the gases containing any ammonia before they are allowed to escape into the open air, *e. g.* from the ammonia-absorbers, the carbonators, the filters, sometimes also from the bicarbonate driers. Then, without removing any precipitate formed on the way, the brine enters the *ammonia-absorbers*, cooled without (p. 25), and is there saturated with cooled ammonia-gas. The gas is then drawn from the absorbers by a vacuum-pump (pp. 31 and 121), but it first passes through one of the brine-washers already mentioned and then usually through a water- or acid-scrubber. The vacuum may here be worked up to 300 mill. of mercury, in order to overcome the pressure within the absorber and the washers, and to extend its action backwards to the ammonia-stills. Any weak washings, other than brine, which are formed here and elsewhere, are best treated in a separate ammonia-still.

The *ammoniacal brine* is now first passed through two or three clarifying-apparatus (p. 28) of sufficient size, and is then thoroughly *cooled* in an extensive set of pipes flushed outside with water (p. 34). It then enters into the *first carbonator* (p. 59), where lime-kiln gas is passed through by means of the blowing-engine up to the formation of normal ammonium carbonate, but no bicarbonate is precipitated. This first carbonator, which is of moderate size, is well cooled, and the liquor running from it is once more cooled down. It is now pumped into the second, large *carbonating-tower* (p. 53), at  $\frac{3}{4}$  or  $\frac{4}{5}$  of its height, and is there saturated with  $\text{CO}_2$  by means of the blowing-engine. The gas issuing from both carbonators, before escaping into the air, is washed with fresh brine and scrubbed with a little sulphuric acid.

The magma of precipitated bicarbonate and ammonium-chloride

solution is now passed on to the *vacuum-filters* (p. 75), which are best placed immediately above the drying-apparatus, so that the drained and washed bicarbonate can be tipped directly into the driers. The filters may be served by the same vacuum-pump as the ammonia-absorbers. The *drying-apparatus* (Thelen pans, p. 88) receive the damp bicarbonate as above and yield it up in the dry state, reduced to normal carbonate (soda-ash). This is either packed at once, or, if it has to be made into dense ash, it is hoisted into *Mactear furnaces*, &c. (p. 97), and is then calcined. The vapours from the drying-pans, containing much  $\text{CO}_2$  and some  $\text{NH}_3$ , are first deprived of most of the water and ammonia by cooling; the weak ammoniacal liquor formed here is, together with similar liquors, distilled separately, as mentioned above. The cooled gas is scrubbed with water or sulphuric acid, and is utilized in the carbonators, mostly after mixing it with lime-kiln gas (comp. *supra*).

The *mother liquor* coming from the vacuum-filters, together with the washings therefrom, is collected in a reservoir, from which it is pumped into the *ammonia-stills* (p. 110). In the upper part of these the ammonium carbonate is expelled by steam alone, in the lower part the fixed ammonia is liberated by steam and lime. The steam is either exhaust-steam from high-pressure engines, or direct boiler-steam, or both. The *waste liquor*, containing  $\text{NaCl}$  and  $\text{CaCl}_2$ , goes into the mud-settlers and is then run away (p. 121). The mixture of vapours issuing at the top of the still is *cooled* by means of coils surrounded by water; the liquor condensing here goes back into the still. The gas issuing from the coolers, consisting of ammonia and some carbonic acid, passes into the ammonia-absorbers, which concludes the cycle of operations.

## CHAPTER VII.

## ANALYSES. COSTS. STATISTICS.

*Composition of Ammonia-Soda.*

Owing to the way in which it is manufactured, ammonia-soda is necessarily much purer than ordinary Leblanc soda not freed from mother-liquor salts. It cannot contain any caustic soda or sulphide, sulphite or thiosulphate; on the contrary, it mostly contains a slight excess of  $\text{CO}_2$ . Iron, alumina, and silica can be found only in extremely small traces, brought in by the tools and in calcining. There is always very little sodium sulphate (*too little for crystal soda, comp. p. 99*). The only impurity worth mentioning is sodium chloride. For many years the factories have guaranteed a "Liverpool test" of  $58^\circ$ , on the Continent 98 to 99 per cent. of real sodium carbonate (*comp. Vol. II. p. 105, on the commercial degrees of soda-ash used in different countries*).

The following analyses were made some years ago, and most of the samples had been weakened by attraction of moisture (or imperfect drying) :—

	Solvay Soda.			English Soda.		Boulouvard's Soda.
	List.	Lunge.	Hanrez.	Pattinson.	Benrath.	Naville.
Sodium carbonate ...	96.23	95.65	99.438	98.72	93.84	94.80
„ chloride.....	0.64	3.22	0.21	0.54	1.17	1.27
„ sulphate ...	0.02	0.31	.....	0.20	0.47	.....
Magnesium carbonate	trace	.....	.....	0.04	0.17	0.09
Calcium carbonate...	.....	.....	trace	0.13	0.16	trace
Ferric oxide .....	}	0.07	{ trace	0.01	0.016	trace
Alumina .....				0.01	0.10	0.09
Silica .....				0.09	.....	
Other insoluble matters .....	.....	.....	.....	.....	0.23	.....
Moisture .....	3.11	0.55	0.31	0.32	3.74	3.75

The *analysis of commercial ammonia-ash* is carried out by the methods described in Vol. II. p. 99, with such deviations as are

caused by its special nature. It is, for instance, unnecessary to test for caustic, sulphide, or sulphite; mostly a simple alkalimetric titration is all that is required. Sometimes it may be necessary to estimate the carbonic acid in excess, by the methods given Vol. II. p. 117, and the ammonia, the latter by prolonged igniting in a current of air and absorbing the gas in standard acid.

"Caustic ash," as frequently sold, especially in France, must be made by special processes from ammonia-soda; such have been described in Vol. II. p. 666. The French soap-makers always insist on such caustic ash; it may be that the small quantity of caustic occurring even in properly calcined Leblanc soda-ash is of much service in fusing-operations, as it increases the fusibility of the mass (comp. *infra*).

Ammonia-soda, from the nature of the process employed, is always *less dense* than Leblanc soda. Ordinary Leblanc soda-ash has an average density of 1.2 (Vol. II. p. 110); ammonia-soda, unless condensed in a special way, only from 0.7 to 0.8. This great porosity of ammonia-soda is no drawback in many operations, but a decided advantage, especially where it must be dissolved for use, as will be easily understood.

But on the whole the lack of density is disadvantageous. Owing to its greater bulk, about half as many more casks are required for ammonia-soda as for Leblanc soda. This not only increases the cost for packages, but in the case of over-sea carriage also the cost of freight, which in this case is not charged according to weight but to the space occupied. This raises the cost of ammonia-soda for transit to America to such an extent that it has led to measures being taken (see p. 97) for artificially condensing ammonia-soda, which, however, never produce quite the same density as that of Leblanc ash. In the European trade this is of less importance, since ammonia-ash is most frequently packed in bags (p. 98).

The objection that ammonia-ash is too porous for *fusion processes* in comparison with Leblanc soda seems to have more force. Glass pots, ultramarine muffles, &c. cannot in consequence of this receive the same amount of charge, hence not so much ammonia-soda can be made in a given space, and much more fuel is consumed, as the conductivity for heat is less with the more porous material. So far as glass is concerned, this drawback, if really a serious one with the old melting-pots, does not exist in Siemens'

basin-furnaces; but no doubt some of the lighter ammonia-ash is here lost through being carried away by the fire-gases.

In the case of ultramarine, the greater porosity is certainly a disadvantage. The mixture for this purpose must be always artificially condensed, and this cannot be sufficiently done with ammonia-soda. Ultramarine makers will not pay so much for it as for Leblanc soda (Curtius, Chem. Ind. 1879, p. 116). Fürstenaud (Chem. Zeit. 1879, p. 441) has given reasons for this. Ammonia-soda, unless artificially condensed, shrinks sometimes 50 per cent. on mere heating by a spirit-lamp; condensed ammonia-ash or Leblanc ash does not do so. Sometimes the shrinking can be prevented by mixing Leblanc ash with ammonia-ash, but this does not always succeed. The shrinking in the ultramarine muffles causes the formation of channels along the sides up to an inch in width, where the air enters and spoils the ultramarine in those places, while the interior of the mass, owing to the bad conduction of heat, remains in an unfinished state.

An objection to ammonia-ash is that its greater percentage of *sodium chloride* unfits it for some uses, *e. g.* for making ultramarine. This may have been true during the first period of the ammonia-soda manufacture, but certainly not since (now for many years) ammonia-ash has been sold with a minimum guarantee of 98 per cent.  $\text{Na}_2\text{CO}_3$ , whereas Leblanc soda formerly contained more than 2 per cent.  $\text{NaCl}$ ! Ilgen (Dingl. Journ. ccxxxii. p. 177) asserts that by adding a little sodium sulphate and by certain manipulations in the mixing of the materials (probably by better compressing them), all the drawbacks of ammonia-soda for ultramarine-making can be removed. As a matter of fact that industry now employs a good deal of ammonia-soda, probably of the densest kind, and Leblanc soda is only preferred for the best qualities of ultramarine.

#### *Cost of Plant.*

For the apparatus formerly used Solvay stated the cost of plant and buildings = £1600 per ton of soda-ash to be manufactured per day. This sum is, however, decidedly too low; at most places about £2400 per ton per day must be reckoned, including the cost of land.

With the old Solvay apparatus each tower made  $2\frac{1}{2}$  tons soda-



ash in 24 hours; a "unit" consists of seven towers (one of which is in reserve), six dissolvers (saturators), six ammonia-stills, and two lime-kilns, producing 15 tons soda-ash per day. The new apparatus at Winnington produce 60 tons per day with one "unit" of plant.

According to a prospectus for erecting a works in conformity with Boulouvard's system near Trieste, the plant for making 4000 tons soda-ash per annum was to cost the following sums:—

	frances.
Apparatus for preparing ammoniacal brine ...	28,000
"    " carbonating      "    " ...	52,000
"    " filtering bicarbonate .....	48,000
"    " calcining      "    " .....	33,000
Grinding the product.....	5,000
Ammonia recovery.....	54,000
Gas- and water-pumps .....	86,000
Steam-boilers .....	21,000
Lime-kilns and belongings .....	11,000
Chimney .....	5,000
Lighting by gas .....	6,000
Workshops .....	10,000
For modifications of the products (?) .....	50,000
Engineer's fee and travelling expenses .....	12,500
	<hr/>
	421,500
Working capital.....	188,500
	<hr/>
	610,000

(I miss, among other items, warehouses, offices, laboratory.)

### *Manufacturing Costs.*

A calculation made by Solvay himself in 1874 for the South of France states the following as the cost of 1000 kilog. (nearly 1 ton) of soda-ash of 57 to 58 per cent. available soda, assuming a yearly make of 3000 tons:—

		frances.		frances.
1942	kilog. rock-salt .....	@ 21	=	40·78
87·5	„ ammonium sulphate. ....	@ 350	=	30·60
2155	„ limestone .....	@ 2·50	=	5·39
1698	„ coals .....	@ 23	=	39·05
250	„ coke .....	@ 40	=	10·32
	Labour .....			15
	Repairs .....			11
	Amortization and general } expenses .....			15
	Casks .....			13·42
				<hr/>
				180·56
	Patent-royalty .....			30
				<hr/>
				210·56
				or about £8 8s.

The principal value of this cost account (which at the time was probably a rose-coloured one!) at present consists in showing the immense progress made since that time.

The following statements refer to Honigmann's plant and to the same period (about 1875).

According to Honigmann's advertisements, the plant for turning out 5 tons of strong soda-ash per diem cost £4500; for 100 parts of soda-ash he required, according to different advertisements (*a*, *b*, *c*) and to verbal statements made to myself in 1878 (*d*):—

	<i>a.</i> 90 p. c. ash.	<i>b.</i> 95 p. c.	<i>c.</i> 98 p. c.	<i>d.</i> 98 p. c.
Rock-salt .....	200	190	175	250
Coal .....	200	175	150	250
Coke .....	.....	.....	.....\	45
Limestone .....	150	140	130	140
Sulphuric acid, 106° Tw. ....	10	8	6	.....
Sal-ammoniac .....	5	4	3	5
Workmen .....	.....	20	.....	.....

There was to be one man per shift at the apparatus, one man at the steam-boilers, two at the centrifugals, three on the day-shift and one on the night-shift at the lime-kilns, one in the day for slaking lime—altogether 11 on the day-shift and 8 on the

night-shift, apart from the yard work, which was done by a contractor with 9 men. The steam-boilers for the above production were equal to 180 H. P.; the ammonia-stills were worked by exhaust-steam.

The statements of Pollaczek, quoted in the first edition (vol. iii. p. 37), will not be repeated here, as his process, although introduced at several places, has been everywhere stopped after a short period of working.

Schreib (Chem. Zeit. 1890, p. 496) states the cost of plant for making 5 tons of soda-ash per day with the simple apparatus sketched by him = £5000, for 10 tons per day = £8000. The manufacturing costs he calculates, on the supposition of "favourable conditions," in two ways, viz. A for cheap salt, B for the case when salt is dear and must be utilized as carefully as possible, which requires more coals and apparatus, and consequently more outlay.

	A.			B.		
	kilog.	at mark.	mark.	kilog.	at mark.	mark.
Salt.....	220	0.40	0.88	180	1.00	1.80
Coals .....	110	0.90	0.99	130	0.90	1.17
Limestone .....	180	0.20	0.36	180	0.20	0.36
Coke .....	25	1.00	0.25	25	1.00	0.25
Ammonium sulphate .....	4	25	1.00	4	25	1.00
Labour and superintendence .....	...	...	1.10	...	...	1.10
Capital, interest, and amortization .....	} ...		0.80	...	...	0.90
Cost of 100 kg. 98 per cent. soda-ash .....	5.38			6.58		
Or per ton, say .....	£2 14 0			£3 6 0		

Later on, Schreib (Chem. Zeit. 1892, p. 693) made the following statements respecting the former and the present quantities of materials used for making 100 kil. of 98 per cent. soda:—

	Formerly.	Now.
Salt .....	250	170 to 240, average 210
Limestone .....	220	150 „ 190, „ 170
Coals and coke...	200	150 „ 190, „ 160
Ammonium sul- phate.....	} 4	1 „ 3, „ 2

Some factories, he says, go down to 1 per cent. ammonium sulphate. The enormous losses to be calculated from Jurisch's analyses of waste liquor, *e. g.* 400 salt to 100 soda, he ascribes to bad sampling; but other figures of Jurisch's, which are extraordinarily low, *e. g.* 160 salt from a French works, are equally fallacious.

In his last paper (Chem. Zeit. 1894, p. 1951) Schreib quotes the following figures, viz. first, those which are the lowest possible according to calculation, secondly those which are the best realized at some places under the most favourable conditions, but nowhere, as he believes, in their totality at any single works:—

Materials for 100 kg. soda.	Calculated.	Used under most favourable circumstances.
Coke .....	6·5 kil.	8
Limestone .....	120 „	170
Lime .....	60 „	85
Salt.....	170 „	190
Coals .....	50 „	90
Ammonium sulphate...	0·75 „	0·75
Limestone gas .....	90 cub. metre	140
Ammoniacal brine.....	0·62 „	0·82
Final liquor (stills) ...	1·20 „	1·70
Horse-power .....	0·7 „	1·1

Upon this he founds the following calculation of manufacturing costs:—

	Price in marks per 100 kil.	Calculated.		Most favourable realized.	
		kilog.	mark.	kilog.	mark.
Salt .....	0·40	170	0·68	190	0·76
Limestone .....	0·20	120	0·24	170	0·34
Coke .....	1·80	8	0·15	14	0·25
Coal .....	1·30	50	0·65	90	1·17
Ammonium sulphate .....	28	0·75	0·21	0·75	0·21
Labour and superintendence ..	.....	.....	0·70	.....	0·60
Repairs .....	.....	.....	0·40	.....	0·40
Sundries .....	.....	.....	0·30	.....	0·30
Amortization .....	.....	.....	0·90	.....	0·90
Management.....	.....	.....	0·50	.....	0·50
Packing.....	.....	.....	0·15	.....	0·15
100 kil. soda cost.....		4·88		5·78	
Or per ton .....		£2 9 0		£2 18 0	

The cost of 100 kil. soda, to be made by Boulouvard's process near Trieste, in 1882, is calculated as follows in the prospectus quoted on p. 135 :—

	per ton.	francs.
175 kil. salt .....	at 10 frs.	1·75
120 „ local coal .....	„ 17 „	2·04
40 „ English coal .....	„ 30 „	1·20
10 „ coke .....	„ 30 „	0·30
80 „ limestone .....	„ 3 „	0·24
25 „ lime .....	„ 15 „	0·37
5 „ ammonium sulphate...	„ 500 „	2·50
		<hr/>
		8·40
Wages for manufacturing and repairs .....		2·25
Packages .....		1·35
Materials for repairs .....		0·25
General expenses .....		0·50
		<hr/>
		12·75

This refers to an annual production of 4000 tons ; for 2500 tons per annum the cost would be 14 frs. per ton. [For that period, 1882, the quantities of materials are assumed much too low, except ammonium sulphate.]

The subjoined costs (p. 140) are taken from the books of a Continental works, where a process similar to Honigmann's is employed ; they refer to 100 kil. 98 per cent. soda.

This synopsis is very remarkable, as showing, from a practical instance, the enormous progress made between 1880 and 1891. But even with their last prices the factory alluded to would be unable to compete nowadays. The following amounts might be assumed for a factory in *good* condition at the close of 1894, supposing the salt to have been bought and therefore more carefully handled than in the case of brine.

1000 kil. 98 per cent. soda require :—

2000 kil. 99 per cent. rock-salt,
850 „ coals (good quality),
1100 „ 98 per cent. limestone,
150 „ coke,
12·5 „ sulphate of ammonia.

## THE AMMONIA-SODA PROCESS.

	1880. Production 4000 tons.			1885. : Production 8000 tons.			1891. Production 10,000 tons.		
	kilog.	at frea.	frea.	hil.	at frea.	frea.	hil.	at frea.	frea.
Ammonia (NH <sub>3</sub> ) .....	1-244	2220	2-74	0-85	1750	1-40	0-75	1180	0-89
Brine .....	.....	.....	0-02	.....	.....	0-03	.....	.....	0-04
Salt .....	16-47	15-50	0-25	23-96	15-50	0-45	0-12	15-00	0-02
Limestone .....	202-19	8-29	1-67	185	5-80	1-08	180-43	4-24	0-76
Coal .....	153-47	18-50	2-85	183	9-50	1-74	79-90	21-02	1-68
Coke .....	53-30	24-00	1-28	53-80	18-50	1-00	44-79	26-00	1-16
Sulphuric acid .....	6-18	40-23	0-24	7-82	37-38	0-29	7-02	32-50	0-23
Wages .....	.....	.....	1-75	.....	.....	1-41	.....	.....	0-99
Repairs .....	.....	.....	1-25	.....	.....	0-80	.....	.....	0-80
General expenses .....	.....	.....	2-00	.....	.....	1-00	.....	.....	1-00
Amortization .....	.....	.....	1-25	.....	.....	1-25	.....	.....	1-25
Packing .....	.....	.....	1-58	.....	.....	0-39	.....	.....	0-35
Total expense .....	.....	.....	16-88	.....	.....	10-94	.....	.....	9-17

	<i>s.</i>	<i>d.</i>
Wages .....	10	0
Repairs .....	7	0
Lighting, Sundries .....	3	0
General expenses (very variable, say) .....	5	0

The cost of *caustic soda* made from ammonia-ash has been stated Vol. II. p. 808.

The Chemical Trade Journal, Nov. 1894 (xv. p. 270), gives a comparison of the cost of ammonia-soda and Leblanc soda in the Lancashire district, which is not of much value, as the quantities are not stated, but only the prices.

	Cost per ton			
	58° ammonia-ash.		55° Leblanc ash.	
	<i>s.</i>	<i>d.</i>	<i>s.</i>	<i>d.</i>
Brine, incl. of pumping .....		9	.....	
Limestone .....	4	6	6	6
Coal .....	9	0	13	9
Coke .....	1	3	.....	
Ammonia .....	6	0	.....	
Wages .....	14	3	14	0
Management, Office-expenses, } Laboratory .....	3	6	2	0
Repairs (wages and materials) .....	5	6	4	6
General expenses .....	14	0	4	6
Saltcake .....	.....		16	8
	<hr/>		<hr/>	
	£2	18 9	£3	1 11

The saltcake is here charged at the extremely low price of 11s. per ton, probably after deducting the value of the hydrochloric acid.

Fassbender (Zsch. f. angew. Chem. 1893, p. 263) calculates the following figures for the horse-power and quantity of steam for manufacturing 10 tons per day:—

	Indicated H.P.	Distillation carried on			
		with vacuum.		without vacuum	
		Steam used.	Steam utilized in stills.	Steam used.	Steam utilized in stills
Lime-kiln gas blowing-engine .....	56.6	kil. 1244	kil. 853	kil. 1538	kil. 1096
Vacuum-pump for stills .....	18	500	322	.....	.....
" filters and calci- ning, brine-pump, sundry engines and friction of shafting .....	40	814	610	1013	783
Water-pump .....	6.4	192	138	236	171
Limestone hoist, milk-of-lime hoist, injector for agitating.....	.....	170	.....	170	.....
Condensation in pipes, &c. ....	.....	250	.....	250	.....
	121.0	3170	1923	3207	2050

(For the principal items in this synopsis special calculations have been given *supra* in the text.)

Schreib (Chem. Zeit. 1894, p. 1950) gives much smaller engine-power for the same production (10 tons), viz. :—

Blowing-engine for lime-kiln gas, 280 cub. ft. per minute, to force against 33 lbs. pressure	20 H.P.
Ditto for calcining-furnace gas, 140 cb. ft. per minute, to force against 37 lbs. pressure ...	12 ,,
Vacuum-pump for filters .....	4 ,,
Water-pump .....	6 ,,
Pumps for brine, milk of lime, &c. ....	2 ,,
Engine for driving the Thelen pans .....	4 ,,
Hoist for limestone and coke.....	2 ,,
Sundry hoists .....	1 ,,
Mill .....	6 ,,
Friction of shafting .....	13 ,,
	<hr/> 70 H.P.

If this power can be supplied by a central condensing-engine, the consumption of coals need not exceed 1 kilog. (2.2 lbs.) per



horsepower-hour, = 1680 kil. in 24 hours; to this we must add 3316 kil. to supply boiler-steam for the ammonia-stills, altogether about 5000 kil. coals. If the stills are worked by the exhaust-steam of the engines, we must (for a counter-pressure of  $2\frac{1}{2}$  atm.) calculate  $2\frac{1}{2}$  kil. (=nearly 5 lbs.) of coals per H.P. hour, that is 3780 kil. The whole of this steam is not required for the stills, but only that for 60 H.P., and the other 10 H.P. can be supplied by a condensing-engine. [This calculation suffers from the error of assuming that all the small machines can be driven from one central engine; but this is not possible, and the exhaust from the small pumping-engines, &c. is practically not available. The above figures, therefore, represent a *minimum*.]

The *repairs* in ammonia-soda works are very considerable, as the ammonia acts strongly upon the iron and all other metals. Even the india-rubber washers, &c. must be frequently renewed. Every "economy" in that line leads to great losses of ammonia. Hence 20 per cent. on the prime cost per annum ought to be charged upon all apparatus in contact with ammonia.

#### *Statistics.*

In England from 1884 to 1893 the following quantities of salt were used for the ammonia-soda process :—

In 1884.....	80,759 tons.	In 1889.....	219,279 tons.
1885.....	115,032 „	1890.....	252,260 „
1886.....	137,220 „	1891.....	278,528 „
1887.....	158,636 „	1892.....	304,897 „
1888.....	212,181 „	1893.....	349,609 „

The production of the largest English firm, Messrs. Brunner, Mond, and Co., increased from 2500 tons in 1875 to 169,000 tons in 1892.

At the Paris Exhibition, 1889, the Solvay Syndicate was stated to manufacture the following quantities :—

In Belgium .....	17,000 tons.
„ France .....	100,000 „
„ England .....	125,000 „
„ Germany .....	100,000 „
„ Russia .....	17,000 „
„ America .....	60,000 „
„ Austria .....	11,000 „
Total.....	430,000 „

These figures, which do not comprise the ammonia-soda made by other firms, are probably considerably "levelled upwards," as referring to that period (the end of 1888). In France, for instance, the official returns show a consumption of 152,202 tons salt in 1887, and of 155,902 tons in 1888 for the *whole* of the ammonia, that is decidedly less than 80,000 tons of soda-ash, and this comprises several small works besides the Solvay. In the French official Chicago Exhibition Report, Haller certainly quotes the production in 1892=110,000 to 120,000 tons for Varangéville, and about 30,000 tons for other ammonia-soda works, such as those near Nancy, Lille, at St. Denis, Sorgues, Giraud.

In 1892 there were the following ammonia-soda works in Germany:—Bernburg, Wyhlen, and Saarlben, all three belonging to the "German Solvay-Works Co."; Grevenberg, Duisburg, Buchau, Heilbronn, Stassfurt, Trotha, Dieuze, Montwy near Inowrazlaw, Salzuffen. The works at Rothenfelde and Pürth had been laid in.

Hasenclever in 1877 calculated the soda manufactured in Germany, expressed as 100 per cent. sodium carbonate, =150,000 tons, three-fourths of which was ammonia-ash. In 1890 he states it =30,000 tons Leblanc soda and 165,000 tons ammonia-soda. In 1894 it was calculated that about 210,000 tons of ammonia-ash (of which the three Solvay works made 125,000 tons) and 40,000 tons of Leblanc ash were made in Germany.

In 1893 there was only one large Solvay factory in America, at Syracuse, producing 82,000 tons of soda, and a few small experimental ammonia-soda works.

## CHAPTER VIII.

## OTHER FORMS OF THE AMMONIA-SODA PROCESS.

*Ammonia-Soda made by Solid Ammonium Bicarbonate.*

SEVERAL former proposals are founded on this method, but it gained a certain measure of success only through the improvements made since 1878 by Schloesing (English pat. 2130, 1878; 2110, 1882; 4025, 1885). The real shape which the process has taken is not very clear from the specifications, and no further account of it has been published; I therefore describe the process from the verbal communications received from Mr. Schloesing on the Paris Exhibition Jury, in 1889, which I have reported in *Zsch. f. angew. Chem.* 1889, p. 695.

Schloesing's new method is founded upon the following procedure:—Beginning with a 9 per cent. solution of  $\text{NH}_3$  in water, and passing in a sufficient quantity of  $\text{CO}_2$ , we obtain a coarsely crystalline precipitate of ammonium bicarbonate. This goes on for a considerable time, and a large portion of the  $\text{NH}_3$  can be precipitated in this manner as bicarbonate. Beginning with a solution of normal ammonium carbonate,  $(\text{NH}_4)_2\text{CO}_3$ , we find, as may be expected, that this does not absorb the  $\text{CO}_2$  as readily as free  $\text{NH}_3$  does. This smaller efficiency of  $\text{CO}_2$  upon a solution of neutral ammonium carbonate is, however, counterbalanced by its more uniform effect. Therefore the large carbonating-towers, and strong blowing-engines connected therewith, may be exchanged for simpler apparatus. The solution of ammonium carbonate is run down in a coke-tower in which lime-kiln gas with 30 per cent.  $\text{CO}_2$  ascends; the gas escaping at the top contains 3 or 4 per cent.  $\text{CO}_2$ . As the towers would otherwise be blocked by solid bicarbonate, two towers are employed in rotation; the weak  $\text{CO}_2$  gas passes up a tower fed with fresh ammonium carbonate, containing a little free  $\text{NH}_3$ , and here dissolves the crusts formed previously on feeding the tower with the second liquor. These

towers are made of wood, 8 ft. 4 in.  $\times$  8 ft. 4 in.  $\times$  26 ft. high. The described way of working them in rotation has been quite successful, so that after two years' work no obstruction had occurred and no cleaning had been necessary. The solution gets heated by the process itself, which prevents a crystallization of ammonium bicarbonate; but even on cooling this would not take place to a great extent, because the saturation is not completed here. This is done in a third apparatus, which receives the tepid solution from the second tower; and here the saturation is completed by *pure*  $\text{CO}_2$ , obtained in the first distillation of the mother liquors running from the sodium bicarbonate.

These mother liquors, as in the Solvay process, contain  $\frac{3}{4}$  of the  $\text{NH}_3$  as chloride and  $\frac{1}{4}$  as bicarbonate. They are distilled in special column-apparatus with 30 chambers; the lime, as usual, enters in the lower third of the height, so that 10 chambers work with lime, 20 with steam alone. On the top a mixture of  $\text{NH}_3$  and  $\text{CO}_2$  escapes, which is condensed in the ammonium carbonate liquor remaining after the crystallization of the bicarbonate. This operation evolves much heat, which is carried away by cold water passing through leaden coils. The work is performed in an apparatus similar to the Glover tower, fed on the top with the mother liquor from the crystallization of the ammonium bicarbonate, while at the bottom the mixture of  $\text{NH}_3$ ,  $\text{CO}_2$ , and steam, almost free from air, coming from the ammonia-stills, is introduced. Here most of the  $\text{NH}_3$  is condensed with but little  $\text{CO}_2$ ; most of the  $\text{CO}_2$ , with a little  $\text{NH}_3$ , escapes at the top and is employed, as previously stated, for the complete saturation of the ammonium bicarbonate solution in the third absorber. In this apparatus the temperature rises to  $40^\circ$  or  $45^\circ$ , and the liquor here turns into a solution saturated at that temperature, so that it crystallizes at once after cooling. The apparatus in question consists of a cylinder with agitating-gear, which is never blocked by the magma of solid ammonium bicarbonate and mother liquor, because the crystals attached to the agitating-blades dissolve on running in the fresh liquor for the next operation.

The ammonium bicarbonate crystals, which are mixed with seven or eight times their weight of mother liquor, are retained in large filters with canvas bottoms till 6 or 7 tons have accumulated; they are then employed directly to decompose  $\text{NaCl}$ , without any washing, by running over them, in the same filter, a suitably dis-

tributed solution of common salt. This, exactly as in the Solvay process, effects a decomposition to the amount of two-thirds; the sodium bicarbonate remains behind in a solid form; the solution running away at the bottom contains the undecomposed  $\text{NaCl}$  ( $\frac{1}{3}$  of the whole), the undecomposed ammonium bicarbonate (also  $\frac{1}{3}$ ), and the newly formed ammonium chloride ( $\frac{1}{3}$  of the  $\text{NH}_3$ ). This reaction absorbs heat, and it is necessary to supply this from without [otherwise, no doubt, no pure sodium bicarbonate would be obtained]. On the filter remains a solid block of sodium bicarbonate, weighing 5 tons, which is there and then washed with water, in order to displace the mother liquor. Before beginning the operation, a large piece of wood had been placed in the centre on the filter; it should now be removed, when it is easy to dig out the crystalline mass. This mass is calcined in an ordinary open furnace, which avoids the well-known difficulties connected with outwardly fired driers and calciners, but of course causes the loss of the second molecule of  $\text{CO}_2$ , which cannot be utilized in this case, being diluted with all the fire-gases. As there is always a little ammonia in these gases, they must be passed through an open scrubber, consisting of a coke-tower fed with sulphuric acid and kept at a temperature of  $100^\circ \text{C}$ ., so that the ammonium carbonate does not solidify but meets the acid in the state of vapour\*.

Schloesing, in his verbal communications, admitted that Thelen pans would be better than his open furnaces; but he considered the latter to be sufficient, as he obtains enough pure  $\text{CO}_2$  from his ammonia-stills. [This reasoning seems to be influenced by the greater cost and the royalty to be paid for the Thelen patent.]

Schloesing claims as a great advantage of his system that it is quite continuous, without the necessity for a periodical cleaning required by the Solvay towers, which, as this must be done by means of hot liquor, always deteriorates the soda made immediately after.

Schloesing states that his apparatus needs only  $\frac{1}{10}$  the mechanical power required for the blowing-engine working Solvay towers; the loss of ammonia is only 0.5 part  $\text{NH}_3$  for 100  $\text{Na}_2\text{CO}_3$ .

\* In this case, and for the special reason stated, a warm condenser may be properly employed here; but this proves nothing for Schloesing's hot condensers in the case of hydrochloric acid, where they are both theoretically wrong and practically a failure. Comp. Vol. II. p. 297.

This process has been introduced by Bell Bros. at Middlesbrough, where 22 tons per day are made by it; a greater extension, it was stated, was avoided in order not to be crushed by the firm of Messrs. Brunner, Mond, & Co. [This consideration has not prevented several others from erecting ammonia-soda works.] Schloesing declares his process to be much cheaper, both as regards cost of plant and working, than the Solvay process. But the latter, with the enormous capital the Syndicate represents in all countries, has a practical monopoly which at present cannot be overcome. When, as Schloesing believes, after a number of years, the patents will have run out and the apparatus used up, newly founded works will prefer his to Solvay's process. [It would be very dangerous to do this on the strength of the published descriptions, for the first French works, after losing £24,000, has been stopped, and the English experiences are kept secret. I have thought it right to repeat the statements of such an authority as Schloesing, although I am far from agreeing with the whole of them. The deterioration of the apparatus hardly counts in this case, for the plant must be written off every 5 years in this process: comp. p. 143.]

The apparatus for filtering the ammonium bicarbonate and converting it into sodium carbonate is shown (according to patent No. 4025, 1885) in figs. 79 to 81. AA are cylinders, two of which can be always put in communication by opening the valves B. In the bottom of each cylinder is a central opening, closed by a lid connected with a hollow wooden pillar C. An opening D on one side of the bottom communicates with box E. Above the bottom there is a grid (not shown in the drawing) covered with canvas. The cylinders have movable covers, whose central openings communicate with box G, through which the charges are divided among the cylinders. The charge must be laid down in the cylinder with great care. After enough ammonium bicarbonate has been put in, the cover of the cylinder is replaced by an apparatus by which the newly added liquor can be very uniformly divided, viz. a circular dish with spirally cut-out bottom, fig. 81. It rests on rollers and has a central bosh, through which passes a shaft, resting on the wooden pillar C and carrying a pulley at the top. Below this the shaft carries a sleeve, to the top of which a second pulley is fixed; below this there is a cup, in the bottom of which from four to eight pipes

Fig. 79.

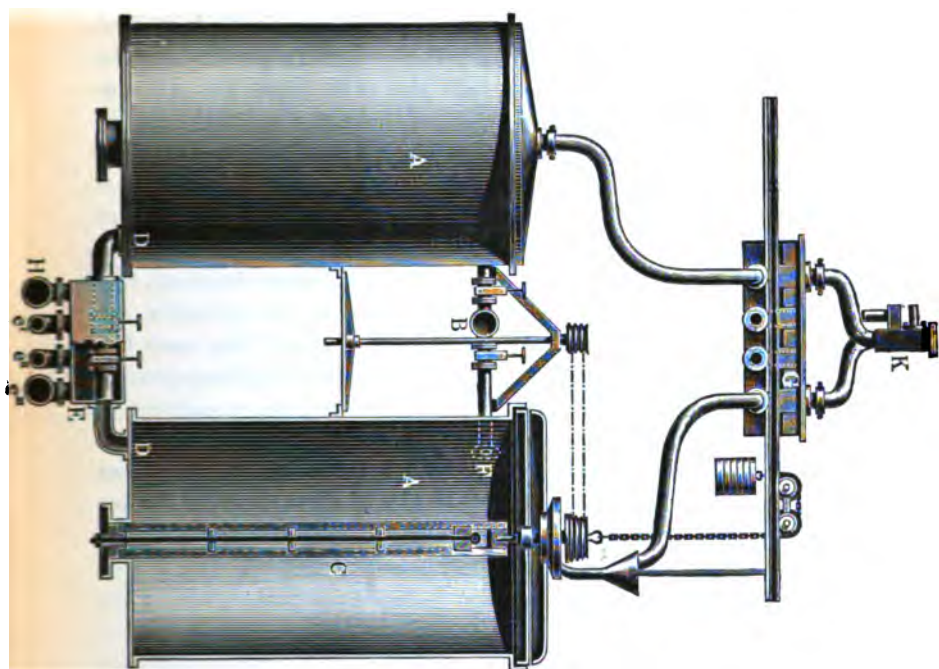


Fig. 80.

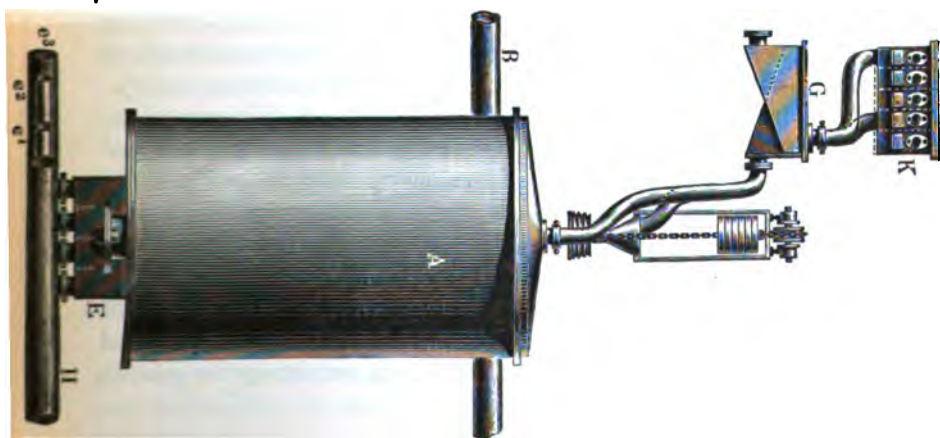
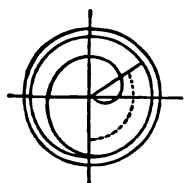


Fig. 81.



are fitted, extending to the outer margin of the spirally bottomed dish. Brine is run into the cup and through its pipes on to the edge of the dish; the pipes and the dish turn in opposite directions. On the inclined bottom of the dish the brine flows as far as the spiral opening, from which it drops upon the crystals with great uniformity. When the decomposition is almost complete, the liquid, issuing at the bottom of the cylinder, is run into another vessel, to be used at the next operation. The same apparatus serves for washing with water. After draining, the central pillar is removed, and the contents of the cylinder are discharged by means of the opening thus produced. The mass has sufficient consistency to be charged into the calcining furnaces.

*The transformation of solid sodium chloride by a solution of ammonium bicarbonate*, a process similar to that just described, forms the subject of Claus, Sulman, and Berry's English patent No. 7701, 1887. They begin with solid NaCl in a vessel similar to Schloesing's, run in a solution of ammonium carbonate, and pass CO<sub>2</sub> into the mass, constantly stirring till the reaction is complete.

#### *Ammonia-Soda in Combination with Coal-gas Manufacture.*

Gerlach (Dingl. Journ. ccxxiii. p. 82) proposed combining the working-up of ammoniacal gas-liquor with the manufacture of soda. The gas-liquor is distilled; in the distillate, chiefly consisting of ammonium carbonate, common salt is dissolved; and CO<sub>2</sub> is passed into it so long as any sodium bicarbonate is precipitated. The liquor now contains some ammonium carbonate (which is distilled off), and ammonium chloride and undecomposed sodium chloride (which must be separated in a suitable manner).

The only "novelty" here is the utilization of the ammonium chloride by sale, instead of by recovering the NH<sub>3</sub>; but this had been proposed several times previously, and it confines the employment of the process to the narrowest possible limits. Besides, Gerlach proposes treating ammonium carbonate with sodium sulphate (comp. the process of Gaskell and Hurter, *infra*). Ammonium nitrate is to be made in a similar manner. The original also contains proposals for separating the chlorides and sulphates of sodium and ammonium by concentrating the solution and crystallizing.



Wallace and Claus (Nos. 272 and 2842, 1877) patented a process intended to combine the purification of coal-gas with the ammoniacal manufacture of soda. The coal-gas is to be purified entirely with ammonia (instead of with lime or iron oxide), which is applied in a series of scrubbers constructed in a peculiar way and fitted with angle-iron bars lying crosswise. The  $H_2S$  is gradually driven out by  $CO_2$ , so that chiefly ammonium sulphide is found in the scrubbers away from, and ammonium carbonate in those near to the retorts; the former even contain an excess of  $CO_2$ , and  $H_2S$  only in the free state. In this liquor common salt is dissolved and pure  $CO_2$  (obtained by decomposing sodium carbonate) passed into it. The precipitate (consisting, as usual, of sodium bicarbonate) is heated in a closed vessel, the  $CO_2$  being collected in a gas-holder and applied as above stated. The solution, containing ammonium chloride, some sodium chloride, and ammonium bicarbonate and sulphide in excess, is heated to drive off the latter, and then run upon heated hydrate of lime: all the  $NH_3$  is thus liberated, and is again admitted into coal-gas, where it starts the purifying process anew. The ammonia contained in the gas is available for other purposes; it is found as ammonium sulphide in the last scrubbers, and suffices for absorbing three-fourths of all the  $H_2S$  contained in the gas. In this process there is a saving, as against the ordinary ammoniacal soda process, of all the carbonic acid and of the ammonia lost.

Calculated from the  $CO_2$  usually contained in coal-gas, each ton of coal employed in the gas-works ought to yield from 70 to 84 lb. of purest soda-ash; the London gas-works alone would produce about 1100 to 1200 tons per week, and the large provincial towns would make this up to 4000 tons.

The ammonia sulphide is partly employed for purifying coal-gas from carbon disulphide; but for the most part it is decomposed by sulphuric or hydrochloric acid, and the (almost pure) sulphuretted hydrogen utilized in the well-known manner. Or the solution of ammonium sulphide is concentrated and treated with sulphurous acid; the ammonium thiosulphate thus formed is decomposed by sulphuric acid, and the sulphurous acid now liberated utilized for the purification of coal-gas from sulphuretted hydrogen, in which case sulphur is precipitated and collected. [This process has not been tried yet. Evidently it has considerable difficulties to surmount; but how far these are fatal, only

experiment could show. The chief point is, whether the resulting liquor is not too impure (tarry) to be used for the direct decomposition of salt.]

*Sodium Monocarbonate and Ammonium Chloride.*

Scherbascheff (English pat. 2271, 1875) patented, in several countries, the following process. By dissolving common salt and ammonium carbonate in the same vessel at from  $60^{\circ}$  to  $70^{\circ}$  C., he professes to obtain almost insoluble [?] monohydrated  $\text{Na}_2\text{CO}_3$  and a solution of  $\text{NH}_4\text{Cl}$ . At a higher temperature than the above the ammonium carbonate would be dissociated into  $\text{CO}_2$  and  $\text{NH}_3$ , and the reaction inverted. He proposes to use the following apparatus:—Two tubs are half-filled with water or brine. In one of these several baskets with salt in lumps are suspended, and the whole heated up to  $60^{\circ}$  C. then other baskets are suspended containing ammonium carbonate. The reaction at once sets in:  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$  is precipitated as a crystalline powder; and  $\text{NH}_4\text{Cl}$  remains in solution. Moreover  $\text{NH}_3$  and  $\text{CO}_2$  are given off, and are conveyed by a pipe in the cover of the vessel into the liquor of the second tub. The operation is finished when the hydrometer shows the liquor to be saturated with  $\text{NH}_4\text{Cl}$ ; then the baskets with salt and ammonium carbonate are taken out and hung in the second tub. The first tub is still heated to  $60^{\circ}$  or  $70^{\circ}$  for some time, in order to precipitate all the soda. The solution of ammonium chloride is run off for crystallization, and the soda taken out of the tub. After centrifuging, washing with boiling solution of soda, and drying, it is ready for sale. The crystallized  $\text{NH}_4\text{Cl}$  is worked up into ammonium carbonate in the well-known way; the mother liquor is employed in the tubs as above.

[This process is wrong in principle, and the details have evidently been worked out by an unpractised hand.]

Another form of this principle was proposed by Dresel and Lentoff (Germ. pat. applic. D 5977). They pass an equivalent of  $\text{CO}_2$  into a saturated ammoniacal brine, cool this down to  $5^{\circ}$  or  $8^{\circ}$  C., and then saturate it with  $\text{NH}_3$  under a slight pressure (about 3 ft. of liquid), so long as a precipitate of  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$  is formed.

*Substituted Ammonia.*

Instead of ordinary ammonia, Bernard (French pat., Oct. 6, 1876) proposes to use methylamine, which, for the manufacture of soda, is certainly far too dear, and does not present any advantage. It is different with the analogous manufacture of *potassium* carbonate from the chloride, since, owing to the great solubility of potassium bicarbonate, the ordinary ammonia process does not apply in this case. For this purpose Ortlieb and Müller (Germ. pat. 5786 and 9376) in 1878 proposed *trimethylamine*, the hydrochlorate of which is extremely soluble, and this process has been actually at work on the large scale for some time. The inventors had constructed the requisite apparatus with much acumen, overcoming the unusually great difficulties presented by the costliness and the frightful odour of the reagent. From their paper on the theoretical part of the process (Bull. Scient. du Département du Nord, 1880, Nos. 7 & 9) it appears that this process is not applicable to soda, as the sodium bicarbonate is not precipitated in a crystalline, but in an extremely fine, almost gelatinous form.

*Alcoholic Ammonia-Soda Process.*

Such a process has been patented by H. de Groussilliers (Engl. pat. 2838, 1873), and has been further developed by him together with W. Siemens and H. Kunheim. As the alleged advantages of this process have proved quite illusory, and it has been relinquished after being used for a short time, I confine myself to referring to its description in the first edition of this work, vol. iii. pp: 47 and 48.

*Application of the Ammonia-Soda Process to  
Sodium Sulphate.*

As Dyar and Hemming's process does not produce hydrochloric acid, it might seem advantageous to work it with sodium sulphate instead of chloride, since in this case the hydrochloric acid has been previously obtained, and the sulphur of the saltcake was formerly reckoned as lost. This is certainly no longer the case since the introduction of the Claus-Chance process, Vol. II. p. 867.

The first mention of this process is found in Bower's patent, No. 8413, in 1840. He mixes in an iron cylinder, provided with agitating-gear, 86 parts of ammonium bicarbonate with 100 sodium sulphate and 200 water for 18 to 36 hours; the solution of ammonium sulphate is then drained from the crystals of sodium bicarbonate. Where ammonium sesquicarbonate is used, a current of  $\text{CO}_2$  is introduced during the agitation. The ammonium sulphate may be decomposed with sodium chloride, and the  $\text{NH}_4\text{Cl}$  used for regenerating ammonium bicarbonate. The sodium bicarbonate is converted into monocarbonate by igniting it in a closed vessel, so that the adhering ammonia can be recovered.

Later on Gerlach again proposed this process (p. 150), evidently without realizing any of its difficulties, and probably without having practically tried it at all. The same must be said of Weldon's patent, No. 5605, 1883.

The process was given a practicable form by Gaskell and Hurter (Pat. 5712, 1883; 8804, 1884; 9208, 1886), who were the first to deal seriously with the question how to dispose of the ammonium sulphate formed in that reaction. If this is mixed with its equivalent of sodium sulphate and heated in a current of steam, the whole of the  $\text{NH}_3$  is liberated and sodium bisulphate remains behind. On mixing the latter with common salt and heating we obtain  $\text{HCl}$  and normal sodium sulphate (saltcake), with which the process is recommenced. The reactions are as follows:—

- (1)  $\text{Na}_2\text{SO}_4 + 2\text{NH}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O} = 2\text{NaHCO}_3 + (\text{NH}_4)_2\text{SO}_4$ ,
- (2)  $(\text{NH}_4)_2\text{SO}_4 + \text{Na}_2\text{SO}_4 = 2\text{NH}_3 + 2\text{NaHSO}_4$ ,
- (3)  $\text{NaHSO}_4 + \text{NaCl} = \text{HCl} + \text{Na}_2\text{SO}_4$ .

The first stage is carried out as follows:—A hot solution of sodium sulphate, of spec. grav. 1.25 to 1.30, is purified from lime, iron, and free acid by adding a little sodium carbonate, and is cooled down to  $38^\circ\text{C}$ . Ammonia is then passed in until 24 or 25 parts  $\text{NH}_3$  are present to 100  $\text{Na}_2\text{SO}_4$ , the temperature to be kept between  $32^\circ$  and  $38^\circ\text{C}$ . At the same time  $\text{CO}_2$  is introduced; when normal ammonium carbonate has been formed, the further introduction of  $\text{CO}_2$  must take place under pressure. As soon as sodium bicarbonate begins to precipitate, the solution is allowed to cool down.

This stage does not seem to offer any great difficulties, but these begin with the second reaction, which is an endothermic one and evidently requires too much time, coals, and steam for an economical process. Blattner (Dingl. Journ. pp. 255, 252) found a great loss of ammonia on heating ammonium sulphate with sodium sulphate; but as he neglected to pass steam through at the same time, the temperature evidently got too high, which explains the destruction of some ammonia.

Hurter and Omholt (Engl. pat. 7107, 1893) describe the following process for working up the ammonium sulphate formed in the above process. They evaporate the solution to dryness in steel boat-pans and mix the dry salt with an excess of *tricalcium phosphate* (natural phosphorite), in order to form monocalcium phosphate, calcium sulphate, and ammonia:—



With this object they heat the mixture in horizontal cast-iron retorts, fired from without, in a slow current of steam superheated to 290°–340° C. The gases are cooled down, whereby a dilute solution of ammonium sulphate is formed, leaving dry  $\text{NH}_3$  for repeating the process. The retort is allowed to cool in an atmosphere of steam down to about 104°, whereby the calcium monophosphate again takes up any expelled water; this residue is then ground up for superphosphate, eventually adding some more sulphuric acid. [This process has therefore only any value if the manufacture of soda is to be combined with that of artificial manure.]

Ortlieb and Müller (Engl. pat. 3967, 1878) suggest converting sodium sulphate into bicarbonate by treatment with  $1\frac{1}{2}$  or 2 equivalents of trimethylamine and carbonic acid.

Wigg (Engl. pat. 7525, 1884) treats sodium sulphate together with a concentrated solution of ammonium carbonate under pressure with  $\text{CO}_2$ . The filtrate from the bicarbonate is to be utilized as ammonium sulphate or to be decomposed by  $\text{NaCl}$  into  $\text{Na}_2\text{SO}_4$  and  $\text{NH}_4\text{Cl}$ .

#### *Treatment of Sodium Nitrate by the Ammonia-Soda Process.*

In 1876 Gerlach proposed sodium nitrate for this purpose (p. 150), and in 1877 Lesage and Co. obtained a patent for it. This process

has been again patented by Chance (Engl. pat. 5919, 1885). He dissolves sodium nitrate in water, adding the alkaline washings from a former operation, and treats the solution with its equivalent of ammonia, then with carbonic acid under pressure. Sodium bicarbonate and ammonium nitrate are formed, the preparation of the latter being the principal object.

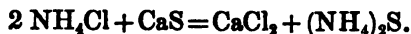
*Employment of Leblanc Alkali-waste in the Ammonia-Soda Manufacture.*

Schaffner and Helbig (Germ. pat. 19216) decompose Leblanc tank-waste with *magnesium chloride*, as this is done in their sulphur-recovery process, Vol. II. p. 858. The sulphuretted hydrogen must, of course, be utilized as there described; but the magnesia formed at the same time is not reconverted into  $MgCl_2$  in the old way (by treating it with calcium chloride and carbonic acid), but it is utilized by employing it, together with an additional quantity of  $MgO$  produced by decomposing the excess of  $MgCl_2$  with lime or dolomite, to expel the ammonia from ammonium chloride,  $2NH_4Cl + MgO = 2NH_3 + MgCl_2$ . This proposal does not seem to have been carried out on a manufacturing scale. It would have to deal with the great, although hardly insuperable, difficulty of completely decomposing ammonium chloride by magnesia.

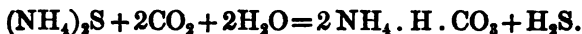
Parnell and Simpson have taken out a large number of patents for a combination of the Leblanc and ammonia process by decomposing the  $NH_4Cl$  produced in the latter with the  $CaS$  produced in the former (Engl. pat. 381, 1937, 7657, 8440, of 1885; 46, 47 of 1887; 5853, 9873 of 1888; 2831, 4648, 6175 of 1888: comp. also Parnell's lecture and discussion thereon in Journ. Soc. Chem. Ind. 1889, p. 11). Their process was very much talked about; it was tried on the large scale, and at first roused serious expectations (*e.g.* Muspratt, Journ. Soc. Chem. Ind. 1886, p. 412), which, however, were not fulfilled, since even the first reaction, viz., the decomposition of tank-waste by the ammonium chloride liquor, is an incomplete one.

As regards the older forms of Parnell and Simpson's process we refer entirely to the patent specifications; and we confine ourselves to an outline of the last-chosen form. By treating ammonium chloride liquor with calcium sulphide in the shape

of tank-waste, ammonium sulphide and calcium chloride are formed :



The ammonium sulphide escapes as vapour, which is absorbed in water or weak ammonia solution, until this titrates 8 to 10 per cent.  $\text{NH}_3$ . This solution is cooled down and treated with pure  $\text{CO}_2$ , which is obtained as below ; thus ammonium bicarbonate is formed and sulphuretted hydrogen is evolved :



The last-mentioned gas is freed from  $\text{CO}_2$  and  $\text{NH}_3$  by washing and is conveyed into a gas-holder for further use. The crystals of ammonium bicarbonate, together with some mother liquor, are removed from the apparatus, and after draining are agitated with brine, whereby sodium bicarbonate is formed (as in Schloesing's process of 1878, p. 146), which is then converted into soda-ash. The ammonium chloride remaining in the mother liquor returns into the cycle of operations by being heated with Leblanc tank-waste. The ammonia removed from the carbonators in the shape of carbonate and mother liquor is made up by adding ammonium sulphate, so that the strength of the ammonia solution is always kept up. The mother liquor from the carbonator serves for absorbing the ammonium sulphide given off in the first operation.

The requisite pure carbonic acid is obtained from lime-kiln gases, after washing and cooling these by absorbing them in a cold aqueous solution of ammonium carbonate, containing from 25 to 30 per cent. of this salt, at a temperature never exceeding  $21^\circ \text{C}$ . Crystals of ammonium bicarbonate are formed which are separated from the mother liquor and heated to  $74^\circ$  in a still, when  $\text{CO}_2$  with a little steam and  $\text{NH}_3$  is evolved. The gas is cooled down, the products of condensation flowing back into the still ; it is then freed from  $\text{NH}_3$  by washing with water or brine, and is then ready for use. The liquid remaining behind in the still is cooled down ; it then gives a second crop of bicarbonate crystals, and the mother liquor returns into the apparatus for absorbing  $\text{CO}_2$  from lime-kiln gas.

Leith (Engl. pat. 21078, 1890) heats brine under pressure with ammonium sulphide and carbonic acid ; sodium bicarbonate, ammonium chloride, and sulphuretted hydrogen are formed. The latter is passed into a mixture of Leblanc waste and water, thus

forming a solution of calcium sulphhydrate (Vol. II. p. 864). This solution is mixed with the  $\text{NH}_4\text{Cl}$  solution filtered from the  $\text{NaHCO}_3$  and heated, when  $(\text{NH}_4)_2\text{S}$  and  $\text{H}_2\text{S}$  escape, and  $\text{CaCl}_2$  remains behind. The ammonium sulphide is absorbed in brine and is used as above; the  $\text{H}_2\text{S}$  is burnt and manufactured into sulphuric acid, or utilized in other ways. [The principal difference between this process and that of Parnell and Simpson seems to be the application of heat and pressure in the first operation.] According to another patent by the same inventor (No. 15648, 1890), the  $\text{H}_2\text{S}$  coming from Parnell and Simpson's process is simply passed into Leblanc waste, the calcium sulphhydrate formed is employed for decomposing ammonium chloride, and the gas evolved used as above.

Ammonium sulphide is also used in a very complicated process by Daguin (Engl. pat. 8668, 1888). The following are the different stages:—1. A mixed solution of  $\text{NaCl}$  and  $(\text{NH}_4)_2\text{S}$  is treated with  $\text{CO}_2$ ;  $\text{NaHCO}_3$  is precipitated,  $\text{NH}_4\text{Cl}$  remains in solution, and  $\text{H}_2\text{S}$  escapes. 2. The  $\text{NaHCO}_3$  is calcined, and yields  $\text{CO}_2$  for No. 1. 3. The  $\text{NH}_4\text{Cl}$  solution is boiled with barium sulphide;  $\text{BaCl}_2$  solution is formed, ammonium sulphide distills off, is absorbed in brine, and used for No. 1. 4. The barium chloride is either brought to dryness, and by  $\text{H}_2\text{S}$  and air converted into  $\text{BaSO}_4$  and  $4\text{HCl}$ , or else these two substances are produced by burning the  $\text{H}_2\text{S}$ , and passing the  $\text{SO}_2$ , together with excess of air, through the solution of  $\text{BaCl}_2$  in the presence of certain metallic chlorides, or else  $\text{BaCl}_2$  is treated with  $\text{MnO}_2$  and  $\text{H}_2\text{S}$ , in order to obtain  $\text{BaSO}_4$ ,  $\text{MnCl}_2$ , and free chlorine. 5.  $\text{BaSO}_4$  is reduced by coal to  $\text{BaS}$ , which is either used in No. 3 or is split up by boiling with water into barium hydrosulphide and barium hydrate. [The aim of this process is to recover the chlorine as such or as  $\text{HCl}$ .]



## CHAPTER IX.

MANUFACTURE OF COMMERCIAL BICARBONATE BY THE  
AMMONIA-SODA PROCESS.

It would at first seem very natural to manufacture the sodium bicarbonate required in commerce, especially for baking-powder and for medical purposes (amounting to about 15,000 tons per annum, comp. Vol. II. p. 720), by the ammonia-soda process, in which that compound is the first product formed. But it has taken many years to effect this, owing entirely to the circumstance that the crude bicarbonate cannot be quite freed from ammonia salts by washing, and it thus retains a smell incompatible with its practicable employment, apart from the loss of ammonia. Koster (Fischer's 'Jahresbericht,' 1880, p. 269) reports that a sample of commercial sodium bicarbonate tested by him in 1880 contained 4 per cent. ammonium bicarbonate! Such stuff could, of course, not compete in the market. Since then, however, that difficulty has been overcome, and most of the bicarbonate now found in trade comes from this source.

The crude bicarbonate, as it remains on the filters, can be converted into the commercial article either by the wet or by the dry method; both have been carried out in practice.

The *wet method* consists in dissolving the crude bicarbonate in warm water, filtering and saturating under pressure with pure  $\text{CO}_2$  at a moderate temperature (below  $65^\circ \text{C.}$ ). On cooling pure bicarbonate crystallizes out and is dried, ground, and packed as described in Vol. II. p. 716. The mother liquors are probably used over again several times; when they have become too rich in ammonia, they are returned into the general manufacture.

Richards (Engl. pat. 376, 1874) adds to crude bicarbonate dilute ammonia, to form neutral ammonium carbonate, which is then removed by washing, whereupon the purified sodium bicarbonate is dried.

Mond and Jarmay (Engl. pat. 2996, 1884) found that on dissolving acid bicarbonate in warm water and cooling, pure bicarbonate crystallizes out and all ammonia salts remain in solution. They dissolve the crude salt at  $65^{\circ}$  C., filter off the insoluble impurities, and allow the solution to cool down. The bicarbonate separates in granular crystals, which are drained by a centrifugal machine or the like, dried, and ground. The solution may also be made at a higher temperature in an atmosphere of  $\text{CO}_2$ , and under pressure, but it must then be cooled down to  $65^{\circ}$  before taking off the pressure. The mother liquors can be used many times over again; when they have become too rich in ammonia, this is driven off by boiling, and the liquid is evaporated to dryness; but preferably the mother liquor is used as a partial substitute for washing the crude bicarbonate on the vacuum-filters (p.78).

Watts and Richards (Engl. pat. 10,955, 1886) remark that in the above process the yield of bicarbonate is small, but it can be increased by adding common salt to the warm solution. The mother liquor is used for dissolving more crude bicarbonate, or instead of brine in the ammonia-soda manufacture.

Solvay (Engl. pat. 173, 1888) treats a hot, filtered, and again cooled solution of crude bicarbonate with pure  $\text{CO}_2$ , obtained by boiling crude bicarbonate with steam in a column apparatus; thus a precipitate of pure bicarbonate is formed.

Jarmay (Engl. pat. 23890, 1893) describes the following improvements:—The crude bicarbonate is dissolved in a closed vessel provided with an agitator and with a valve-funnel for charging the salts; by means of a close steam-coil the temperature is kept between  $85^{\circ}$  and  $90^{\circ}$  C. The escaping vapours, containing  $\text{NH}_3$ , some  $\text{CO}_2$ , and steam, are passed through a multitubular cooler, where they are surrounded by mother liquor from a former operation, and from which the cooled  $\text{CO}_2$  is carried away for use. The solution remaining in the dissolver now contains bicarbonate and sesquicarbonate; it is passed through a filter-press and then pumped upon an iron tower, containing many compartments with inner water-cooling pipes, which reduce the temperature to  $72^{\circ}$  C. At the bottom lime-kiln gas is introduced and causes a constant agitation by bubbling through the liquid. The carbonated liquor, filled with suspended bicarbonate, is conveyed from the bottom of the tower on to a filter, placed on a higher level, where the solid bicarbonate remains behind; the mother liquor first flows round

the pipes of the above-mentioned apparatus, where it is heated, and then back into the dissolver. The bicarbonate crusts forming in the tower are dissolved by mother liquor, heated to 80°, and this solution is also conveyed back into the dissolver, to be saturated with crude bicarbonate.

In the *dry method* the principal feature is drying the damp, crude bicarbonate in an atmosphere of  $\text{CO}_2$ , to avoid decomposition, and depriving the escaping vapours of their ammonia. This may be done by the following apparatus, which is somewhat similar to that used in drying wool:—Within a large closed box is an endless double chain, running in several tiers one above another, iron plates between the two chains acting as carriers. The damp bicarbonate is first put into a horizontal revolving drum, fixed alongside the box, through which passes the mixture of gases coming from the drying-box, and from this onto the top tier of the box, from which it descends gradually to the bottom, and is there carried outwards. Warm air, or better warm lime-kiln gas, is blown into the box by means of a fan-blast; it travels over the single tiers, and lastly through the aforementioned drum. This warm air is best not introduced at the bottom tier, but higher up, so that the warm dry bicarbonate cools down to some extent before leaving the apparatus. In the top of the drying-box is an opening through which pure  $\text{CO}_2$  is introduced; this, owing to its high specific gravity, sinks to the bottom, and causes especially the lowest tiers to be always filled with an atmosphere saturated with  $\text{CO}_2$ , so that decomposition of the bicarbonate is prevented. The vapours leaving the apparatus are conveyed through a cooler, and finally through a scrubber, to recover the ammonia contained therein. Perfectly white, inodorous bicarbonate is obtained in this way.

Gaskell (Engl. pat. 11775, 1884) patented heating bicarbonate in an atmosphere of  $\text{CO}_2$ , to remove the ammonia.

Jarmay (Engl. pat. 23889, 1893) dried moist bicarbonate, obtained according to patent No. 23890 (p. 160), in a long covered trough, with inlet and outlet valves for the salt at opposite ends, and a conveying-shaft provided with paddles. At one end enters air previously heated up to 95° C., which is drawn through the apparatus by means of a fan-blast acting in a vertical tube just over the outlet valve. The bicarbonate dust carried along by the fan-blast collects in a chamber, closed by a dust-bag. Both the

inlet and outlet valves for the salt are so constructed as to form a hermetic seal. The drying air is preferably mixed with  $\text{CO}_2$ , and may then be brought to a higher temperature, which may be done by a multitubular apparatus surrounded by steam.

Wood (Engl. pat. 8958, 1888) makes the crude bicarbonate into a paste with water, and places it in a horizontal cylinder provided with safety-valve, agitator, steam-coil, and a perforated pipe connected with a blowing-engine. The temperature is kept at about  $93^\circ \text{C}$ . by the steam-coil. Air is blown in, keeping the pressure at  $2\frac{1}{2}$  to  $3\frac{1}{2}$  atmospheres by means of the safety-valve, and this forced circulation of air and heating is continued "till all oxidizable substances are oxidized and all volatile impurities are driven out." Now cold water is made to circulate through the coil, and carbonic acid is forced in, instead of air, in order to saturate the product again. [This process appears to be neither good nor economical.]

#### *Sodium Sesquicarbonate.*

This name, which is not quite appropriate, has been given to a product manufactured by a process of Watts and Richards (Engl. pat. 13001, 1886). It is  $\frac{2}{3}$  carbonate or "urao,"



(comp. Vol. II. p. 52), and is obtained by allowing a solution containing 2 mol.  $\text{CO}_2$  to 3 atoms Na to crystallize at a temperature not below  $35^\circ \text{C}$ . A solution of the proper composition is obtained either by heating sodium bicarbonate until it has lost  $\frac{1}{3}$  of its  $\text{CO}_2$ , and dissolving the residue in hot water, or by mixing a hot solution of 84 parts  $\text{NaHCO}_3$  with 106 parts  $\text{Na}_2\text{CO}_3$ . The clarified solution is allowed to cool slowly, with stirring; the sesquicarbonate deposits in good crystals, which are separated from the mother liquor and dried. The product does not effloresce; it is easily soluble and well adapted for wool-scouring, as flannel does not shrink with it (Journ. Soc. Chem. Ind. 1887, p. 700).

Cl. Winkler has obtained splendid crystals of the same product from mother liquors in making ordinary soda crystals from ammonia-soda (Zeit. f. angew. Chem. 1893, p. 446; comp. p. 100).

## SECOND BOOK.

# VARIOUS PROCESSES OF THE ALKALI MANUFACTURE.

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WE shall now enumerate the various proposals for manufacturing alkali, not arranging them according to the chronological order of the inventions or their practical value; but we shall now and then, where this is useful and possible, pronounce an opinion as to their importance.

The subject will be divided according to the various substances from which soda can be extracted, beginning with cryolite, which still serves as the basis of an actual manufacture; to be described in detail, and then enumerating more or less succinctly the various processes in which sodium chloride, sodium sulphate, sodium nitrate, and soda-felspar are employed.

## CHAPTER X.

## THE MANUFACTURE OF SODA FROM CRYOLITE\*.

THE mineral *cryolite* was found for the first time at Ivitût, in South Greenland, by a Danish whaler, who brought a piece of it to Copenhagen, without stating where it came from. It was first described by Schumacher, in 1795, and analyzed by Abidjaard, more correctly by Klaproth, who proved it to contain soda—the first time that this alkali had been found in the mineral kingdom otherwise than as common salt. Further analyses by Vauquelin, Berzelius, and Deville completely established the composition of the mineral. The original occurrence of the mineral in Greenland was discovered by Giesecke after long seeking (1806–1813). Up to 1849 it was only found in scientific collections; but in 1849 Professor Julius Thomsen at Copenhagen proved cryolite to be easily decomposable by lime both in the dry and in the wet way, and showed its applicability to the manufacture of soda. In 1854 he obtained an exclusive right (till 1884) of mining for cryolite and working it up in Denmark for soda and alumina; this right was afterwards sold to a company. The first small factory was built in 1857, at Copenhagen; the first large one, still existing, at

\* The most complete description of this industry is that by Banzon, in Hofmann's 'Bericht,' 1875, i. p. 660. Other, but partly antiquated, sources which have been consulted are:—Wagner's 'Regesten,' p. 57, and 'Jahresberichte' for 1862 and 1868; Knapp's 'Chemische Technologie,' 3rd ed. i. 2, p. 471; Wurtz, 'Dictionnaire de Chimie,' ii. p. 1557; E. Kopp, 'Schweizer Ausstellungs-Bericht,' 1873, iii. p. 20; Goldschmiedt, 'Oesterr. Bericht,' 1877, vii. p. 12; the English patent-specifications, and my personal observations at the old cryolite-soda works at Golschmieden near Breslau. In 1890 I also visited the Natrona Works near Pittsburg; but neither that visit nor the description published by the Pennsylvania Salt-manufacturing Co. during the Chicago Exhibition in 1893 has added anything new to the above.

Oeresund near Copenhagen. In 1861 and later on, factories were erected at Harburg, Mannheim, Prague, Goldschmieden near Breslau, and Warsaw. All the latter works have had to discontinue the use of cryolite, since the Pennsylvania Salt-manufacturing Company at Natrona near Pittsburg, in 1865, obtained a right to two-thirds of all the cryolite produced (*in maximo* 6000 tons per annum) up to 1884. In 1855 H. Rose proposed this mineral for the manufacture of aluminium.

On the whole, from 1856 (when first whole cargoes were shipped) to 1873, 68,000 tons of cryolite were obtained; since 1865, about 6000 or 7000 tons per annum.

All cryolite comes from Ivitût, from a valley on the south side of Arsuk Bay, where summer lasts three months. Some of the mineral is found below low-water mark, but in a more impure state. On the mainland there is a bed of 30,000 square feet of white cryolite lying above impure mineral. Any mineral containing more than 20 per cent. impurities is rejected. The purest is 10 feet below the surface; below 15 feet it becomes very dark, and at last almost black; but on igniting the latter, it also becomes white. The impurities are galena, copper-pyrites, spathic iron-ore, fluor-spar, and lime-spar; the surface is covered with clay and sand. The working takes place chiefly from April to the end of December, and to a certain extent even during the remaining months.

Pure cryolite is a semitransparent, snow-white, glassy mineral; in the impure state it is yellow or reddish. Its specific gravity is 2·953, its hardness 2·5 to 3. The crystals are very indistinct; but the mass has a good cleavage along the faces of a square or oblong prism. It is easily fusible, and in a glass tube shows the reaction of fluorine. It is incompletely soluble in hydrochloric acid, completely in concentrated sulphuric acid, and is also decomposed by lime. Its chemical formula is  $\text{Al}_2\text{F}_6 \cdot 6\text{NaF}$ ; in the pure state it would contain:—

Aluminium	13·07,	corresponding to alumina .....	24·54
Sodium	33·35	„ soda ( $\text{Na}_2\text{O}$ ) .....	44·79
Fluorine	53·58	„ hydrofluoric acid..	56·44

---

100·00

For *working up* cryolite into soda and alumina many processes

have been proposed, only one of which is carried out in practice, viz. the dry treatment with calcium carbonate: this will be described more fully now; and the others will be briefly mentioned afterwards.

The present process was discovered by Thomsen in 1850; he was undoubtedly the originator of the entire industry (Dingler's Journal, clxvi. p. 441); and all other works have been laid out after his plan. The process is founded upon the fact that, on igniting cryolite with calcium carbonate, carbonic acid escapes, and calcium fluoride and sodium aluminate remain behind:



Both the cryolite and chalk are finely ground by edge-rollers. To 100 cryolite 150 chalk is employed, instead of 127 as required by the formula; the excess of chalk makes the mass more porous and less fusible. In spite of the finest grinding and mixing of the materials, a portion of the cryolite inevitably becomes surrounded by the sodium aluminate formed, by which its decomposition is prevented. Later on Hagemann and Jörgensen succeeded in avoiding this drawback by adding to the mixture some of the impure calcium fluoride obtained in the process itself. This causes more consumption of fuel, and requires twice the number of furnaces, but increases the yield from 12 or 13 per cent. alumina and 60 alkali to 18 per cent. alumina and 68 or 70 alkali.

A proper temperature is of great importance for this process. The decomposition begins below a red heat; but in practice the latter must be attained in order to complete it. The melting-point of the mixture is not very much higher; so that there is only a short range between the two. The mass, being a bad conductor of heat, must be in a thin layer. If it gets to the melting-point, much cryolite is protected from decomposition, and the lumps formed are very difficult to lixivate. Hence ordinary reverberatory furnaces are not applicable, because in these the heat is too unequal, and one portion of the mixture would be fluxed before the other was decomposed. [Mechanical furnaces like those employed in black-ash and saltcake making and carbonating would no doubt do the work most completely.] The furnace constructed by Thomsen, which avoids the above-mentioned drawback, has the shape shown in figs. 82 to 85. The furnace-bed, C, is made of fireclay lumps 18 inches square and 3 inches thick;



Fig. 82.

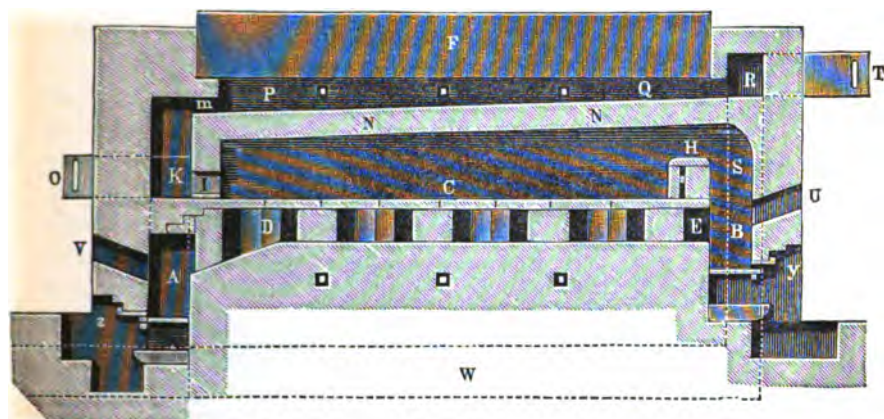


Fig. 83.

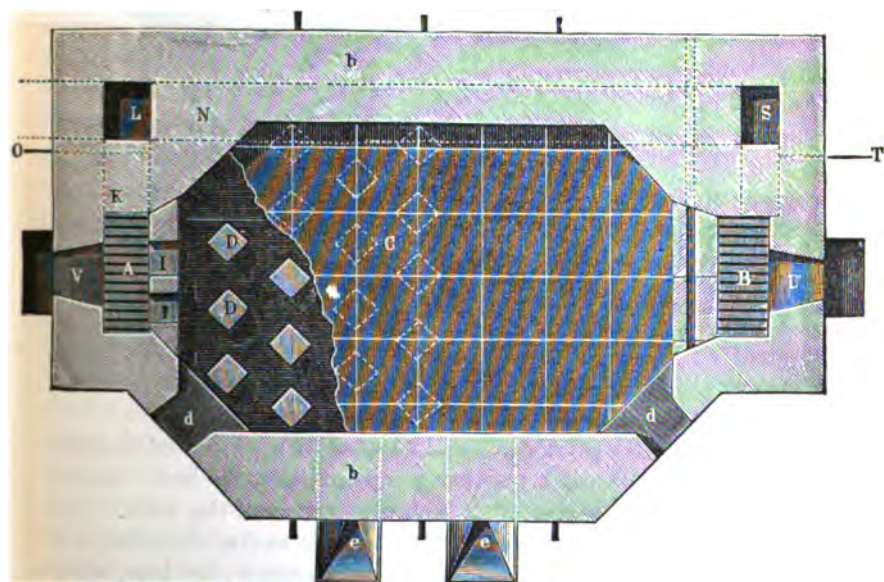


Fig. 84.

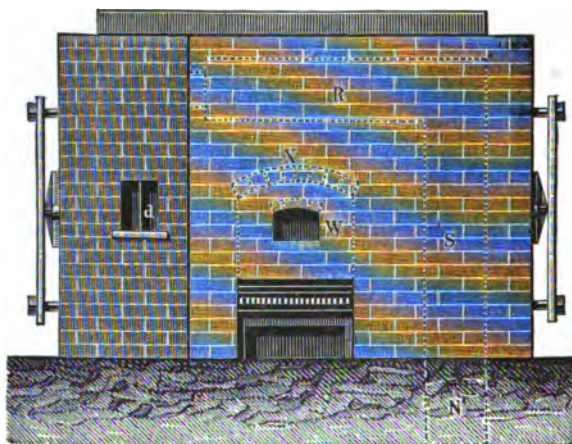
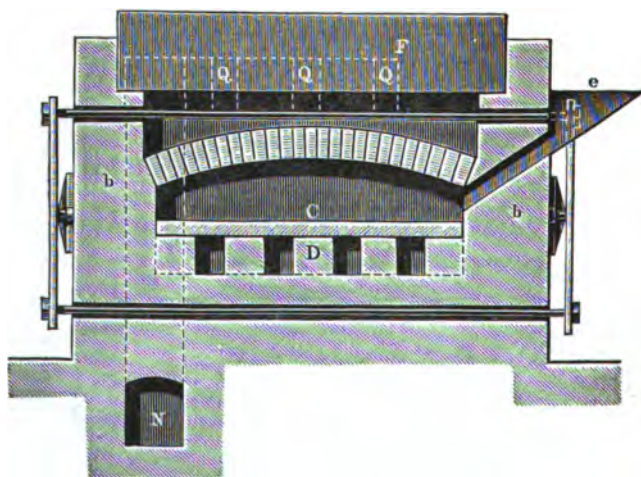


Fig. 85.



they rest upon 9 × 9 inch pillars 12 inches high, so placed that the flame of the fireplace A is uniformly divided below the bed. Round the sides the lumps rest on 2-inch projections of the walls. The lower flue DE, which is consequently as wide as the whole bed, and 12 inches high, at E joins into the second fireplace, B; here, below the fire-bridge H, the lower level rises up so that the flue is only 5 to 6 inches high. The united flame of both fires now travels over

the bed towards the snore-holes I I, and through these into the flue K. The latter communicates, 1st, with the flue L, which joins the main flue N, but it can be cut off by the damper O; 2nd, with the opening *m*, which admits the flame into the space P between the arch and the pans F. The draught is then continued by the snore-holes Q Q Q into the horizontal flue R, leading into the main flue past the damper S. When the damper T is shut, and O opened, the flame passes from the furnace directly into the main flue, without heating the pans; but when O is shut and T opened, the draught passes beneath the pans. The two fire-grates are of equal size, 3 feet long and 15 inches broad; the grates are composed of 1½-inch wrought-iron bars; the stoke-holes U and V are closed with fireclay slabs. The front wall of the fireplace W, 18 inches thick, is independent of the side walls and is carried on iron girders *y* and *z*, and closed by an arch X. By this arrangement it can be easily renewed without disturbing the other brickwork. The bridge H is cooled by an air-channel S, which has small openings at the side of the fireplace B. The side walls *b b* must have very secure foundations. The arch is 9 inches thick; the joints of the bricks run parallel with the long side of the furnace. The furnace is cased in metal plates 3 × 2 feet, bound together by uprights and tie-rods; that nearest the flame from *m* is protected by an iron or earthenware pipe. Cleaning-holes are provided for the flues K, R and the space below the bed between the pillars. The hopper *e* serves for charging the furnace. The furnace-bed has an area of about 100 square feet; it is 13 feet long and 8 feet wide. It is charged every two hours with 10 cwt. of mixture, daily with 6 tons of mixture, corresponding to 2½ tons cryolite. [This is not the mixture containing calcium fluoride.] The fuel consumed amounts to about 16 cwt. coals per diem, which also suffices for the evaporation of the soda-liquors to the crystallizing-point, and ultimately for drying the limestone on a metal plate. In this furnace the mass becomes red-hot all through, but no portion of it melts; so that it can be easily lixiviated. According to Thomsen, the decomposition of the cryolite is so nearly complete that from 100 parts of pure mineral 197 parts of crystal soda are obtained, the theoretical yield being 204 parts. [This statement, which is made for working without calcium fluoride, is directly contradicted by the above-quoted statements of Hagemann and Jörgensen; according to Bing (Wagner's Jahresb. 1862, p. 235), from 100 cryolite 175 soda

crystal are obtained, with a consumption of 37·5 coals.] If any lumps have been formed in spite of proper working in the furnace, they must be separated from the fine powder by riddling, and put back into the furnace with the next charge.

At Natrona 50 parts of finely ground and sifted cryolite are mixed with 10 parts of limestone and 40 of quicklime, and the mixture is ignited in 16 Thomsen furnaces, built back to back. Each charge amounts to  $9\frac{1}{2}$  cwt., and after igniting weighs  $8\frac{3}{4}$  cwt.; six charges are made per day [of 12 hours]. The mass is kept at a red heat for two hours, then drawn out and cooled on brick floors and sent to the lixiviating-apparatus.

The charge drawn out of the furnace is put while still hot into the lixiviating-tanks, made of wood, tapering below and provided with a perforated false bottom. The lixiviation is commenced with dilute liquors and mother liquors from former operations. The heat of the mass itself raises the temperature of the liquid; at last hot water is employed. The strong liquor shows  $60^{\circ}$  Tw.; the weaker liquor is employed for the next operation. At Natrona iron tanks ( $9 \times 5 \times 3\frac{1}{2}$  feet) are used, and a liquor of  $48^{\circ}$  Tw. is obtained by using hot water containing sodium aluminate with a little carbonate and caustic; the lixiviation is finished with cold water, by which weak liquors are obtained. Sodium aluminate is dissolved out and pumped into the apparatus for treating it with carbonic acid; the residue, of a reddish colour, is principally calcium fluoride (formed in the operation), mixed with calcium carbonate, undecomposed cryolite, a little ferric oxide, and a little sodium aluminate. Its composition, according to Hagemann, is the following [but evidently the waste was examined after having been acted upon by the carbonic acid of the air] :—

	per cent.
Calcium fluoride .....	62·01
„ carbonate .....	11·89
„ oxide .....	5·62
Potassium carbonate .....	0·37
Sodium „ .....	3·94
Magnesia .....	0·93
Silica .....	3·78
Ferric oxide .....	5·00
Alumina .....	5·00
Moisture .....	1·45

At first this waste was only used for mending roads; but it is now considerably employed, partly for new mixtures (from which it is of course always recovered again), partly for bottle-glass: it makes the glass-mixture more easily fusible, permits a larger addition of lime, and thus yields stronger glass. Unfortunately the silicium fluoride acts too much upon the furnace-materials; so that no more than from 6 to 9 per cent. of the calcium-fluoride waste is put into the mixture. The glass retains 1.75 to 2.75 F; 1 per cent. of the fluorine volatilizes in the furnaces. The same waste furnishes a bluish-white enamel on stoneware and majolica. It is also used as a flux for metallurgical purposes, and as an admixture to fireclay for fire-bricks; these bricks are very hard, and resist the moisture very well.

The solution of *sodium aluminate*, which is brown, but free from iron and strongly alkaline, is sometimes boiled down to dryness and sold. There is, however, but very little sale for it; endeavours to introduce it into glass-making, calico-printing, &c. have failed. The liquor is therefore generally decomposed by forcing in carbonic acid, in closed horizontal boilers with agitators, 5 feet diam. and 60 feet long; and thus a precipitate of hydrated alumina (containing some soda) and a solution of sodium carbonate are obtained. The formula usually given is



This, however, is not correct; for a real compound of 45 per cent. alumina, 20 per cent. sodium carbonate, and 35 per cent. water is precipitated in a finely granular readily settling state. The precipitate can be almost entirely deprived of soda by long washing with boiling water; but this makes the alumina gelatinous and difficult to treat. When it has been washed down to 2 per cent. soda, it is dried on a brick floor by means of steam-pipes which are soon protected against rusting by a coat of dry alumina, thus also protecting the bulk of the alumina against contamination with iron. If alumina is to be sold as such, it must be washed down as well as possible; otherwise, if sulphate is to be made from it, it is merely separated from the adhering liquor by centrifuging or by a vacuum-filter and at once mixed with dilute sulphuric acid, in which it dissolves readily, especially when heated to 110° C. The solution of aluminium sulphate is boiled down in copper pans to the consistency of treacle, and poured into moulds, in which it

solidifies into porcelain-like slabs, which are sold as *concentrated alum*. The alumina in it varies from 12 to 20 per cent.; the latter strength can only be obtained from cryolite. The usual formula  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$  requires 15.31 per cent.  $\text{Al}_2\text{O}_3$ . According to the mode of manufacture, both the alumina and the aluminium sulphate are almost entirely free from iron; and the latter is also easily obtainable free from an excess of acid. The strongest (20 per cent.) aluminium sulphate can be obtained in a porous form, greatly assisting its solubility, by stirring among the mass cast into the moulds, just before solidifying, a little sodium bicarbonate, from which  $\text{CO}_2$  escapes at this temperature and causes the tough cake to be honeycombed by innumerable bubbles, like fermenting dough. This "Natrona porous alum cake" is much in favour with American consumers.

The sodium aluminate may also be converted by Loewig's process into caustic soda and "colloidal" alumina.

The *carbonic acid* is always employed in the shape of lime-kiln gas, purified from dust by a long string of pipes and by scrubbing in coke-towers. The lime-kiln serving for this purpose at Goldschmieden is illustrated and described in the first edition, vol. iii. pp. 61 to 64; but it is much more to the purpose to refer to the more modern kilns, described in connection with the ammonia-soda process in this volume p. 37 *et seq.*

With a proper arrangement of the lixiviation the hot solution of *sodium carbonate* separated from the precipitated alumina is concentrated enough to crystallize on cooling; sometimes it must be first evaporated in pans on the top of the cryolite-furnace. At Natrona it is boiled down to  $60^\circ \text{Tw.}$ , and in winter run into the coolers to crystallize, but in summer into enormous reservoirs, holding up to 1000 tons of soda, made of cast-iron plates, where it remains through the winter. In spring the mother liquid is pumped out and the crystals dug out with ordinary mining-tools. The mother liquor can always be used again in the process, as it contains very little impurities. The crystal soda from cryolite is extremely pure; it contains at most  $\frac{1}{4}$  per cent. of sodium sulphate, and it was usually assimilated to the common English soda by adding a little sulphate, to obtain harder crystals (p. 99). By treating it with quicklime, caustic of 75 per cent.  $\text{Na}_2\text{O}$  can be made from it. Some calcined

cryolite-soda analyzed by Tissandier (Monit. Scient. 1868, p. 909) contained :—

Moisture .....	2·06	3·28	4·61	0·89
Sodium carbonate...	88·97	95·20	91·68	93·22

The Pennsylvania Salt-manufacturing Company consumes annually 6000 tons of cryolite.

*Treatment of Cryolite with Lime in the wet way.*—This process, already indicated by Thomsen, was subsequently patented in England by Spilsbury (June 19th, 1856), who, however, never carried it out. In the same year Tissier (Wagner's Jahresb. 1857, p. 395) took it up; but he could only decompose one third of the cryolite in this way. Sauerwein proved (ib. 1862, p. 299) that complete decomposition can be attained by employing 6 molecules of lime (=836 parts) to one molecule of cryolite (=447 parts). The same has been found by Hahn (Hofmann's 'Bericht,' 1875, i. p. 638), who gives some special prescriptions for the process, as well as Sauerwein. The latter worked in a complicated manner, which is of little interest now, as it has not stood the test of practical experience.

Wagner (his Jahresb. 1863, p. 343) proposed decomposing cryolite by baryta; but this is far too expensive to have any prospect of realization.

Schuch (Ann. Chem. Pharm. cxxvii. p. 61) proposed boiling cryolite with caustic-soda liquor, by which it is dissolved with formation of sodium aluminate and sodium fluoride. This never has been and is not likely to be carried out in practice.

Bauer (Germ. pat. 54824) proposed decomposing cryolite by boiling with its own weight of calcium carbonate, with 1 per cent. soda and 30 to 40 parts of water.

Lauterborn (Germ. pat. 14495) decomposes cryolite by boiling with water alone; sodium fluoride is dissolved and aluminium fluoride remains behind, in a state fit for the manufacture of alumina.

Persoz (Ann. Chim. Phys. May 1859, p. 109) proposed the decomposition of cryolite by sulphuric acid, which was actually tried at Copenhagen, but given up again. To 1 molecule of cryolite, =476 parts, 6 molecules of sulphuric acid, =558 parts,

are required, or 642 parts of ordinary strong vitriol, diluted with water. The products are aluminium sulphate, sodium sulphate, and hydrofluoric acid :



The great expense of vitriol, the evolution of HF, the difficulty of separating the sulphates of aluminium and sodium, and the small value of the latter, make this process altogether worthless.



## CHAPTER XI.

THE MANUFACTURE OF SODA DIRECTLY FROM  
SODIUM CHLORIDE.*By Electrolysis.*

THIS subject is treated in the fourth book of this volume.

*By Steam.*

Sheridan (No. 7426, 1837) patented the decomposition of common salt in the state of vapour by steam "or hydrogen" at a bright red-heat. He figures an apparatus consisting of two conical furnaces; the inner one serves for receiving the salt and introducing the steam, the outer one for forming and removing the alkali and the vapour of HCl.

Swinburne (No. 8134, 1862) patented the same thing; and so did Gillard (No. 1790, 1861, and No. 1914, 1865); steam of 1000° C. was to be employed, and introduced into the melted salt through platinum tubes.

Powers and Dale (patent No. 91, 1863) propose the same, but hope to assist the decomposition by adding oxide of iron, aluminium, or manganese.

Henry (for Laurent) obtained provisional protection, No. 3340, 1865, for decomposing melted sodium chloride by superheated steam.

Weldon, No. 2768, 1866, patented the same, along with the decomposition of sodium fluoride or nitrate by steam, indicating special heating-appliances.

Cabot (Chem. News, xxxi. p. 243) describes laboratory experiments on decomposing common salt by superheated steam; he obtained hydrochloric acid and alkaline ashes. Evidently the reaction  $2 \text{NaCl} + \text{H}_2\text{O} = \text{Na}_2\text{O} + 2 \text{HCl}$  had taken place; but "of

course the yield was no approach to the theoretical one, and it could not be applied as a technical process."

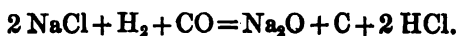
Similar experiments were made by Viedt (Wagner's *Jahresb.* 1875, p. 383) without any practical result; but he did not abandon all hope of final success.

The action of steam comes into play in an "invention" by Sir Francis Bolton (pat. No. 14866, 1884), according to which caustic soda and hydrochloric acid are to be made from common salt by mixing it with barium or strontium sulphate, and heating in an atmosphere of steam. HCl escapes; the residue is stated to consist of "a mixture of sodium or barium (or strontium), with an equivalent of oxygen and an equivalent of SO<sub>4</sub>, together with undecomposed salt and earthy sulphate." On lixiviating caustic soda is obtained, and a residue of barium (or strontium) sulphate, which can be used over again.

Spring (Ber. d. deutsch. chem. Ges. 1885, p. 345) makes the following statements as to the behaviour of steam towards a mixture of 10 molecules NaCl with 1 molecule NaOH:—At 140° C.: no action. At 245°: a short evolution of HCl. At 350° to 410°: slow evolution, soon ceasing. At 500°: steady evolution of HCl. During a treatment, for one hour and a half, of NaCl with steam (probably at 500°) 6 per cent. was converted into NaOH; by 12 hours' treatment, and several times grinding up, 12 per cent. A mixture of NaOH with up to 6 mol. NaCl evolves no HCl whatever on fusion; up to 6 NaCl there is a slight, at 10 NaCl a very distinct evolution of HCl.

We have seen (Vol. II. p. 476) that the decomposition of sodium chloride by water is a strongly endothermic reaction, which, even with strongly overheated steam, can be effected only to a very limited extent. It is not impossible that at extremely high temperatures, such as may be attained by burning hydrogen, perhaps also by burning water-gas, or by electricity—in the former case by the action of the highly-heated steam in the nascent state—sodium chloride may be decomposed in a more complete way, and I expressed this opinion years ago before professional men.

Mills (Engl. pat. 4661, 1891) states that he is able to utilize *water-gas* in a different manner: If *water-gas* is passed through sodium chloride, kept in fusion in a converter, sodium oxide, carbon, and hydrogen chloride are formed:



The residue of sodium oxide and carbon is utilized either for preparing metallic sodium by further ignition, or for preparing anhydrous sodium oxide by burning the carbon, or for manufacturing caustic soda by treatment with water. [I cannot understand how the sodium chloride is to be kept in the state of fusion in the converter, and where the large amount of heat necessary for the reaction is to come from.]

*By Oxygen.*

Martin (French pat. 231895, 1893) prescribes decomposing sodium chloride by oxygen in the "dissociated" state. He employs a furnace with five wrought-iron or fire-clay retorts, with an outside coating of magnesite. Within these cylinders there is a porous cylinder made of magnesia, leaving an annular space round the sides of the retort. In this space the NaCl is volatilized at a red heat, and the vapour is exposed to oxygen or to air free from carbonic acid. Chlorine is evolved, and soda is left behind in the retort. [Evidently quite impossible.]

*By Potash.*

Bergmann seems to have been the first who proved that a solution of common salt can be decomposed by potash, and who found that, on evaporating a mixed solution, first a crop of potassium chloride and then one of sodium carbonate are obtained. The first explicit description of this process was given by the Court-apothecary Meyer at Stettin, in 1784. The same plan was recommended by Samuel Hahnemann, Wiegleb and Westrumb, Kastelleyn and Remler (Wagner's 'Regesten,' p. 16). In England Loesh manufactured soda at Walker-on-Tyne from 1802 to 1815, according to Lord Dundonald's patent of 1795, in this way:—Equal parts by weight of Russian potash, at £40 per ton, and common salt were dried in a furnace, mixed with slaked lime and small coal and melted in a reverberatory furnace. The product was lixiviated and boiled down until, on cooling, a crop of potassium chloride could be obtained. After a second crop of the same had been separated, the mother liquor was evaporated to dryness, the residue ignited and dissolved for making soda crystals. From 40 cwt. of a mixture of salt and potash 20 cwt. of potassium

chloride and 20 cwt. of "British ash" were obtained, or, instead of the latter, 30 to 40 cwt. of crystal soda. The "British ash" was sold at from £16 to £20 per ton, the crystal soda as "potash-soda." The crystallization took place in small shallow lead vessels, only during the winter months.

To this category also belongs the process of Bischof (Dingl. Journ. iv. p. 380), who tried to make sodium bicarbonate by passing carbonic acid gas into an aqueous solution of equal parts of potash and common salt: sodium bicarbonate was separated; and potassium chloride remained in the mother liquor.

It is hardly necessary to mention that with the present relation of the prices of potash and soda such processes are entirely out of the question.

Weldon (Engl. pat. 980, 1881) proposed precipitating sodium bicarbonate from a mixed solution of  $\text{NaCl}$  and  $\text{K}_2\text{CO}_3$  by means of  $\text{CO}_2$ . The  $\text{KCl}$  remaining in the mother liquor was to be treated with  $\text{MgO}$  or  $\text{MgCO}_3$  and  $\text{CO}_2$ ; potassium magnesium carbonate is precipitated, which is decomposed by boiling with water into  $\text{MgCO}_3$  and  $\text{K}_2\text{CO}_3$  (*vide* p. 181).

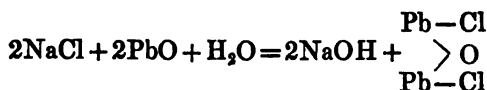
*By Lime.* (Wagner's 'Regesten,' p. 16.)

Scheele, in 1773, noticed that from a damp mixture of common salt and lime soda effloresces in the air after several weeks' time. Probably independently of Scheele, this observation was also made by the French chemists Proust, Pelletier, and Deyeux. On the strength of the latter, Guyton-Morveau and Carny, in 1782, obtained a French patent for soda-making which was actually worked for some time, but with little success, at Croisic in Picardy.

From a solution of common salt a solution of calcium bicarbonate precipitates sodium bicarbonate. Apparently this reaction explains the formation of soda efflorescences in soils containing common salt.

*By Lead Oxide.*

In 1773, Scheele noticed that common salt is decomposed by litharge. A solution of common salt, filtered through a layer of litharge, became caustic, and in the air yielded carbonate. The reaction is as follows:



This observation was published by Bergman in 1775. Kirwan reports that soda was made in England by this process already in 1782, and the yellow residue (of lead oxychloride) was employed as a pigment. The latter was patented as the principal thing in 1787 by Turner, and has retained the name of Turner's yellow ever since; the caustic soda was only a by-product in this case. Göttling (1781) and Achard (1784) knew the process and pronounced against it. In 1792 it was patented in France in the name of Curandau; and it emerges again in 1793 in the report of the Comité du salut public as the process of Chaptal and Bérard, who had favourably judged of it. We have already mentioned that this was the process first employed by Losh at Walker. There 50 parts of finely ground litharge was gradually mixed with  $12\frac{1}{2}$  parts of common salt dissolved in 55 parts of water, always leaving the mixture at rest for some hours, till a white crust had formed; this was first broken up and mixed with the mass before new brine was added. After two or three days the batch was finished; the caustic soda was lixiviated with water and the yellow residue melted and sold as a pigment; or, as this could not always be done, the lead was melted from it again at considerable loss. According to Clapham (Chem. News, xxi. p. 148), by this process, in the *best* case, only 5.6 per cent. of the salt was decomposed, which only with the then very high price of salt could leave any margin of profit. The patent of Watt and Tebbutt, No. 7538, 1838, quotes this process again, but prescribes boiling the lead oxide and common salt together. A patent of J. Hunt's (No. 8056, 1839), if it has any meaning whatever, belongs here. According to it, common salt was to be ground up with granulated metallic lead or zinc. Anthon, of Prague, pronounced a favourable opinion on the litharge process, on the strength of experiments on the small scale. In 1866 (No. 2077) Rowbotham obtained provisional protection for the original process of Scheele; but the matter was first taken up again seriously in 1869, by Bachet (pat. No. 939, 1869, and No. 2401, 1870), whose process was tried in 1870, on a pretty large scale, at the same Walker works which had formerly belonged to Losh. This trial, however, was soon dis-

continued. The principal difference of Bachet's process from the previous one consisted in his adding slaked lime: 5 cwt. of a mixture of 100 litharge, 70 common salt, and 50 slaked lime was ground in a mill with a little water. Decomposition sets in at once; caustic soda, lead chloride, and hydrated lead oxide (which, it is remarkable, does not act on salt) are generated; but only 19 to 20 per cent. of the salt is decomposed. The white pasty mass is strongly pressed; and the clear solution of caustic soda and common salt that runs off is ground with fresh quantities of slaked lime and lead oxide. Thus gradually 47 to 50 per cent. of the salt can be converted into caustic soda. The solution pressed off at last is filtered through a layer of calcium hydrate in order to deprive it of any dissolved lead compounds, and concentrated by evaporation, during which the greater part of the NaCl is separated and can be fished out. Caustic soda with 70 per cent.  $\text{Na}_2\text{O}$  could thus be produced. The chief thing, however, has still to be mentioned, viz. the regeneration of the lead oxide; and upon this the process was wrecked. The cakes of  $\text{PbCl}_2$ ,  $\text{Pb}(\text{OH})_2$ , unchanged  $\text{PbO}$ , and  $\text{Ca}(\text{OH})_2$  remaining in the press were first heated to  $173^\circ \text{C}$ . in order to convert the  $\text{Pb}(\text{OH})_2$  into  $\text{PbO}$ ; and the mass was then introduced into boiling lime-water, in which the  $\text{PbCl}_2$  also was transformed into  $\text{PbO}$ ; the residue was again employed for decomposing common salt. The filtrate could be almost entirely deprived of the lead which it still contained by cooling and crystallizing, followed by addition of common salt. But apart from the fact that this regeneration could not be carried out without a considerable loss of lead, the recovered lead oxide frequently proved much less active than fresh litharge—probably because much calcium and lead carbonate was formed, which not only are inactive towards common salt, but even seem to interfere with the action of lead oxide. After prolonged trials, the process had to be given up as useless (Chem. News, xxi. p. 148).

*Zinc oxide* has been proposed for the same object, but without any better success.

The litharge process was taken up again by Knab (No. 3082, 1877). Common salt is to be mixed with its equivalent of litharge; five times its weight of water is to be added, and the heat raised by means of steam to  $70^\circ$  or  $80^\circ \text{C}$ . In a few hours the decomposition is complete. The mass is deprived of the largest portion of its caustic soda by hydraulic pressure, and the

remainder of the soda obtained by stirring up the lead chloride with water and repeatedly pressing it. The  $\text{PbCl}_2$  is instantaneously decomposed by stirring up with its equivalent of ammonium carbonate and water, a solution of ammonium chloride and lead carbonate being formed. The latter is sold as such, or reconverted into  $\text{PbO}$  by ignition, whilst the  $\text{CO}_2$  given off, along with the  $\text{NH}_3$  evolved from the sal-ammoniac, again forms ammonium carbonate. In order not to lose the chlorine, the ammonium chloride is not decomposed by lime, but by manganese protoxide,  $\text{NH}_3$  and  $\text{MnCl}_2$  being formed. The latter by heating with access of air is converted into  $\text{Mn}_2\text{O}_3$ ,  $\text{Cl}$  becoming free. As the  $\text{Mn}_2\text{O}_3$  does not decompose  $\text{NH}_4\text{Cl}$ , it is reconverted into  $\text{MnO}$  by heating with sulphur,  $\text{SO}_2$  being formed at the same time. This process, extremely complicated in its last part, is founded upon reactions several of which have long been proved extremely incomplete, and consequently has no technical value whatever.

The Société anonyme Lorraine industrielle (Germ. pat. 23791; Engl. pat. 4144, 1882) separates the lead chloride from the caustic soda by alcohol, and regenerates metallic lead from the chloride by white pig-iron.

Romiquières (Engl. pat. 14977, 1888) fills two communicating boilers two-thirds full with finely divided lead. Into one of these he runs a concentrated solution of caustic soda, containing a little sodium sulphate, until the lead is just covered, raises the temperature, and injects air at a pressure of three or four atmospheres. Then the solution is forced over into the second boiler, where the process is continued, until all the lead has been converted into a solution of sodium plumbite,  $\text{Na}_2\text{PbO}_2$ . By treating this with  $\text{NaCl}$ , he obtains a precipitate of  $\text{PbCl}_2$  and a solution of  $\text{NaOH}$ , twice as much as had been originally employed. By injecting  $\text{CO}_2$  during the treatment with  $\text{NaCl}$ ,  $\text{Na}_2\text{CO}_3$  can be obtained. [What is to be done with the lead chloride?]

#### *By Ammonia and Carbonic Acid.*

This is the ammonia-soda process, treated in Book I.

#### *By Magnesia and Carbonic Acid.*

(Weldon's patent, No. 629, 1866.)

A mixture of common salt, cold water, and magnesia or magnesium carbonate is saturated with carbonic acid under pressure in

a closed vessel, with or without agitation. Soluble magnesium bicarbonate is formed, which at once decomposes its equivalent of NaCl, MgCl<sub>2</sub> being formed and remaining in solution, whilst NaHCO<sub>3</sub> is precipitated. The solution of MgCl<sub>2</sub> is evaporated to dryness, the residue ignited, the HCl driven off and condensed, and the MgO recovered for use. The NaHCO<sub>3</sub> is calcined so as to obtain Na<sub>2</sub>CO<sub>3</sub>. Weldon expected the hydrochloric acid generated to cover all expenses, and to obtain the soda gratis. The reaction would be :—



Wagner (Jahresb. 1873, p. 256) declares this process to be the most perfect of all soda-making processes; it would be better to say "it would be" the most perfect, if all the reactions went on as smoothly as in the equation; but this is far from being the case. That process is useless for manufacturing soda, but it has been taken up by Engel for manufacturing potassium carbonate. In this connection Weldon took out another patent (No. 980, 1881), in which he proposes to saturate a solution of NaCl and K<sub>2</sub>CO<sub>3</sub> with CO<sub>2</sub>, to separate the solution of KCl from the precipitated sodium bicarbonate, and to reconvert the KCl into K<sub>2</sub>CO<sub>3</sub> by MgO and CO<sub>2</sub> (p. 178).

Lanquetin (Engl. pat. 3846, 1881) returns to Weldon's process of 1866, simply substituting dolomite for pure magnesium carbonate, and thus rendering the process even more impracticable.

Carthaus describes an improvement of Weldon's process (Germ. pat. 79221). In order to prevent the precipitation of basic magnesium salts, it is preferable not to treat the sodium chloride and magnesia at the same time with water and carbonic acid under pressure, but to add NaCl or saturated brine in equivalent proportion to a solution of magnesium bicarbonate, previously finished. It is best to add a little ammonium salt to the sodium chloride and to work with concentrated solutions. The sodium bicarbonate and magnesium chloride formed are treated in the well-known manner.

An additional patent (No. 81103) prescribes employing the magnesium chloride solution over and over again, until it is saturated with MgCl<sub>2</sub>, whereupon it is to be worked up for MgO.



*By Carbonic Acid.*

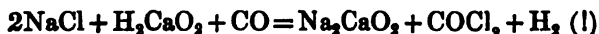
Hugo Müller (Deutsch. chem. Ges. Ber. iii. p. 40) noticed that  $\text{CO}_2$  is somewhat more soluble in water containing  $\text{NaCl}$  than in pure water, a little  $\text{NaCl}$  being decomposed by  $\text{CO}_2$  and  $\text{HCl}$  being liberated; the latter can be proved by the destructive action of the  $\text{HCl}$  upon ultramarine.

As early as 1866 Carl Funck, as he reports in the Chem. Zeitg. 1879, p. 660, had proposed to manufacture soda by the action of liquid  $\text{CO}_2$  on  $\text{NaCl}$ , by injecting gaseous  $\text{CO}_2$  into a saturated solution of  $\text{NaCl}$  below  $0^\circ \text{C.}$ , under a pressure of 36 atmospheres. The precipitated sodium bicarbonate is filtered under the same high pressure, and from the solution the  $\text{CO}_2$  and  $\text{HCl}$  are successively distilled off. [A criticism of this "invention" seems unnecessary.]

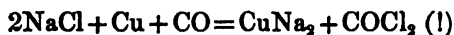
Lancaster (Engl. pat. 4122, 1879) injects steam, heated to  $800^\circ \text{C.}$ , into limestone, and passes the mixture of  $\text{CO}_2$  and hydrogen which he believes is formed thereby into fused sodium chloride; thus soda, chlorine, and  $\text{HCl}$  are said to be generated.

*By Carbon Monoxide and Dioxide.*

Benze and Hardtmuth (Germ. pat. 73935, 74937, 74976) prepare caustic alkali and chlorine from alkaline chlorides by heating with  $\text{CO}$  and  $\text{CO}_2$ . They employ an iron cylinder, widening out below, with a plumbago lining, standing on a cast-iron basement. The bottom is formed by a flat cone, resting on the same basement, with an edge reaching down into a spout arranged below the iron shell. At the centre of the bottom cone enters the tuyere of a blowing-engine. The top of the furnace is closed and provided with a ground-in charging-door; below this there is a pipe for taking away the chlorine, all lined with plumbago. The lower third of the apparatus is filled with charcoal or coke, the upper space with a mixture of charcoal or coke and salt. The coal is burnt by means of the blast entering at the bottom; the sodium is converted into carbonate and the chlorine is set free. The alkaline carbonate formed collects in the bottom spout; the chlorine escaping at the top ought to have at least a temperature of  $600^\circ$ . If lime is added in this process the reaction is represented to be :



According to a further patent (No. 75272) a metal, or coal and a metal, are to be added to the salt, in which case, *e. g.*, an alloy of copper and sodium is formed, from which copper and caustic soda are obtained by lixiviation with water :



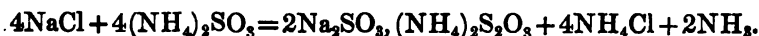
The English patent of Duryee (No. 5457, 1880) already mentions the decomposition of common salt mixed with coal-dust in a revolving cylinder by means of a hot blast, alkali-chlorine being formed.

*By Coal and Sulphuric Acid.*

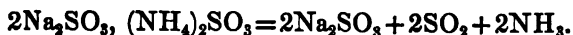
W. Robinson (Engl. pat. 10080, 1885) mixes salt, coal-dust, and sulphuric acid intimately, heats the mixture in a furnace, and treats the gaseous mixture for recovering the  $\text{HCl}$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{S}$ , as well as the solid residue "according to well-known methods" for the recovery of sodium bicarbonate, carbonate, sulphur,  $\text{H}_2\text{S}$ , &c. [Criticism unnecessary.]

*By Sulphurous Acid and Ammonia.*

Tauber (Germ. pat. 43921) treats a saturated solution of sodium chloride, applying cold, with the necessary quantity of ammonia and sulphurous acid, to form a sodium-ammonium sulphate :



The greatest portion of the double salt is precipitated and is separated by a centrifugal machine from the ammonium chloride. It is then heated to  $110^\circ \text{C}$ . ;  $\text{NH}_3$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{O}$ , are volatilized and are again passed into  $\text{NaCl}$ , and neutral sodium sulphate remains behind :



The latter is decomposed by lime, calcium sulphite being obtained as a "by-product."

*By Phosphoric Acid.*

Delhay (Engl. pat. 4371, 1887) decomposes calcium phosphate by hydrochloric acid, adds to the mixture sulphuric acid, filters the solution from the precipitated calcium sulphate, heats the mixed solution of phosphoric and hydrochloric acid with  $\text{NaCl}$

till all HCl has escaped, and converts the monosodium phosphate formed at 200° C. by boiling with lime into caustic soda and tricalcium phosphate [?].

*By Lead or Zinc Pyrophosphate.*

Margueritte, Nos. 394, 2700, 1854, patented the following process. NaCl is heated with lead or zinc pyrophosphate ( $\text{Pb}_2\text{P}_2\text{O}_7$  or  $\text{Zn}_2\text{P}_2\text{O}_7$ ). Sodium pyrophosphate is formed, which remains behind, whilst  $\text{PbCl}_2$  or  $\text{ZnCl}_2$  is volatilized and condensed in chambers. The sodium salt, dissolved in water and boiled with lime, yields a solution of NaOH and a precipitate of  $\text{Ca}_2\text{P}_2\text{O}_7$ . The precipitate is again boiled with the previously condensed metallic chlorides, and yields a solution of  $\text{CaCl}_2$ , which is run to waste, along with a precipitate of lead or zinc pyrophosphate, which is again employed for decomposing. The caustic soda can, if required, be converted into carbonate by a current of carbon dioxide (!).

*By Sodium Phosphate.*

Arrott (patent No. 2446, 1872) dissolves trisodium phosphate ( $\text{Na}_3\text{PO}_4$ ) in water, and treats it with  $\text{CO}_2$  or  $\text{NaHCO}_3$ ; disodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) and  $\text{Na}_2\text{CO}_3$  are formed, and separated by fractional crystallization. The  $\text{Na}_2\text{HPO}_4$  is again converted into  $\text{Na}_3\text{PO}_4$  by melting two equivalents with a little more than one equivalent of NaCl. As No. 2236, 1873, Arrott obtained provisional protection for a process of making soda-ash and chlorine by igniting ferric phosphate with common salt, with the assistance of air and steam. The HCl escaping is condensed as usual; the residue contains  $\text{Fe}_2\text{O}_3$  and sodium phosphate, which is dissolved out and decomposed by lime into caustic soda and calcium phosphate; the latter serves for again producing ferric phosphate with the  $\text{Fe}_2\text{O}_3$  dissolved in the hydrochloric acid. [Criticism of these proposals seems quite unnecessary.]

*By Sodium Metaphosphate*

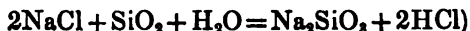
(according to Siebel, Deutsch. chem. Ges. Ber. viii. 1786).

Sodium metaphosphate is melted with sufficient  $\text{NaNO}_3$  in a retort-like vessel, so that along with escaping nitric acid, which is condensed as usual, a basic salt is formed; this is treated with a

little water, afterwards with  $\text{CO}_2$ ; sodium carbonate and phosphate are formed, dissolved out, evaporated to  $77^\circ \text{Tw.}$ ; a concentrated solution of ammonium carbonate is added, the whole allowed to cool, and the microcosmic salt,  $\text{Na}(\text{NH}_4)\text{HPO}_4$ , crystallized out. Thus about two-thirds of the soda remains in solution as carbonate, along with a little microcosmic salt.  $\text{CO}_2$  is passed through the solution, whereupon  $\text{NaHCO}_3$  is precipitated; the mother liquor is added on dissolving the next bath of basic sodium phosphate. The microcosmic salt is pressed off and heated, the  $\text{NH}_3$  volatilizing is again worked up for ammonium carbonate, and the remaining metaphosphate employed as above. The inventor of this remarkably complicated and unpractical-looking proposal sees no essential difficulty in it, except the selection of a suitable material for the vessels, as which he proposes plumbago.

*By Silica and Steam.*

On melting, common salt does not unite, but the latter melts much sooner than the former, lies as a cover on the silica, and evaporates before the latter can come into action. Only in minimal quantities and quite superficially does combination take place—for instance, in the salt-glazing of earthenware; but here the salt acts in the state of vapour, and the reaction is probably only made possible by the aqueous vapour existing in the fire-gases. In order to utilize this reaction on a large scale, steam must be applied to begin with. Already, in 1809, Gay-Lussac and Thénard founded upon this a proposal for soda-making. Blanc and Bazille (No. 8386, 1840) obtained an English patent for this process, which they intended to carry out in this way:—280 parts of common salt and 200 of sand, intimately mixed, are loosely put into horizontal cast-iron cylinders, entirely surrounded by the flame, and heated to a cherry-red. Through the axis of each cylinder passes a wide tube, perforated with many holes, for introducing steam; at the end of this tube a wide porcelain or stoneware pipe carries off the vapour of  $\text{NaCl}$  and  $\text{HCl}$ . The steam must enter equably and slowly, so that the temperature shall never sink below a cherry-red heat; in that case the decomposition of the mixture into neutral sodium silicate and hydrochloric acid (according to the formula

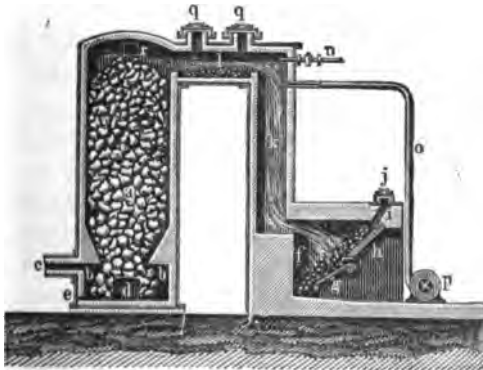


becomes easy and complete [?]. The exit-tube for the gases ends in a wide chamber for depositing the volatilized salt, which is then continued into an apparatus for condensing  $\text{HCl}$ ; this, however, must work at a very low pressure. The neutral sodium silicate obtained as above is very slightly soluble; consequently it can be deprived of undecomposed common salt by crushing and washing, and by melting with two-thirds of its weight of soda is converted into soluble basic water glass. The latter is drawn out hot into cold water, dissolved, and, by a current of  $\text{CO}_2$  from a lime-kiln, decomposed into sodium carbonate and gelatinous silica. The latter can be employed for the manufacture of fine glass. It is evident that this process is useless: for each 100 parts of crude silicate 60 parts of soda-ash are sacrificed; and afterwards, on washing the gelatinous silica, undoubtedly much soda is again lost, —all this independently of the difficulties in decomposing the salt.

Fritsche in 1858 obtained an Austrian patent for converting common salt into soda by means of silica and steam; no particulars are stated (Wagner's Jahresb. 1858, p. 118).

In England the same process has been the subject of several patents; the only one, however, which in the beginning promised to become successful was that of Gossage (No. 2050, 1862). He employed a peculiar apparatus, sketched in fig. 86: *a* is a tower

Fig. 86.



made of fire-bricks, tapering near the bottom and then widened out again; it is nearly filled with pieces of quartz or flints; at the

bottom at *b* a space remains free, which communicates with the flue *c* for taking away the gases. More quartz can be thrown in through the opening *d*, which is usually closed. The melted sodium silicate can flow away through the opening *e*. In the gas-generator *f* coals are burnt with insufficient access of air, so that combustible gases are formed; *g*, grate-bars; *h*, slanting fire-plate; *i*, charging-hopper; *k l*, gas-flue; *n*, pipe for introducing steam; *o*, pipe for introducing air compressed by the fan-blast *p*. The bottom of the flue *l* is charged with salt through the openings *q q*. Through *r* more quartz can be put in. By means of the generator *f* and the fan-blast *p* a very great heat can be produced in the tower *a*; when this has been attained, salt is put in through *q q*, which volatilizes and, by the assistance of steam from *n*, decomposes the hot quartz; sodium silicate is formed, together with hydrochloric acid, which escapes from *c* with the residual gases and is condensed [not very readily!]. The sodium silicate is employed for glass-making or as water glass; or it is decomposed by means of  $\text{CaO}$  into  $\text{NaOH}$ , or by introducing  $\text{CO}_2$  into  $\text{Na}_2\text{CO}_3$ . The same apparatus may be charged with alumina instead of quartz, and sodium aluminate obtained (see below)—or with clay, or clay-slate, or felspar, granite, &c., in which cases mixtures of sodium silicate and aluminate are obtained.

The latter Gossage probably never realized; but he certainly made sodium silicate for some time in the manner described, and exhibited soda obtained from it in Paris in 1867. At what cost it was obtained was not stated; so much is certain, that the process had to be given up entirely: the apparatus could not resist the enormous heat; the decomposition was very incomplete, and the  $\text{HCl}$  difficult to condense.

Brisse endeavoured to improve Gossage's process by heating salt to the melting-point on the sloping bottom of a reverberatory furnace, adding silica in the state of fine powder, and conducting superheated steam through the mass. "The sodium silicate thus obtained is treated with calcium carbonate at a high temperature and the mass lixiviated, whereby sodium carbonate and calcium silicate are obtained, from which silica is separated by hydrochloric acid" (sic!) "and used over again."

Whilst the processes just described are evidently useless, a proposal made by Ungerer (Dingl. Journ. cxvii. p. 343) does not seem entirely impracticable. He proposes to get the mixture of

salt and sand, by means of steam and heat, up to the fritting-point, and then to employ it for glass-making; he does not even mention any possible use of the frit for soda-making, which no doubt its slight solubility would prevent.

As a curiosity it may be mentioned that, as No. 447, 1854, Cowper (for Laureau) patented the decomposition of natural or artificial silicates by six months' "*fermentation*" with alternate layers of straw, sawdust, &c. After that time the mass was to be impregnated with thick milk of lime and calcined in a furnace; on lixiviation it was to yield very pure soda; and the residue was to be employed as pozzuolana!

Williams again (No. 5406, 1881) patents the decomposition of sodium chloride vapour by steam and silica.

Sanderval (Compt. Rend. cxvi. p. 41) heats sodium chloride with silica in porous clay retorts to obtain sodium silicate and chlorine.

Martin (French pat. 210676) heats nitre-cake (acid sodium sulphate) with small coal and cinders from coal fires in an iron retort to a red heat: there are formed sodium silicate and  $\text{SO}_2$ ; the latter is to be converted by red-hot coke into carbon bisulphide, and other products of this kind; the sodium-silicate is to be converted into caustic by lime. Sodium chloride is also to be treated with blacksmith's cinders, gelatinous silica, and lime, to obtain sodium silicate and volatile ferric chloride.

A very peculiar process has been patented by the celebrated inventor of the basic steel process, S. G. Thomas (prov. prot. No. 5849, 1883), which process can hardly be taken seriously. Lumps are to be formed from sodium or potassium chloride with additions of ferric oxide, manganese oxide, magnesia, lime, and calcium chloride. These are placed in a converter; fused pig-iron, containing little carbon, but at least 4 per cent. silicon, is to be run in and the mass is to be treated with a current of air or of steam, superheated at least to  $300^\circ \text{C}$ . Chlorine escapes and a slag remains, consisting of alkaline silicate mixed with a little ferric oxide.

#### *By Boric Acid.*

Böhme found, in 1848 (Wagner's 'Regesten,' p. 23), that boric hydrate decomposes common salt, in the presence of steam, into sodium borate and hydrochloric acid. The former might be converted by lime into caustic soda and calcium borate, and from the

latter the boric acid regenerated [no doubt by  $\text{HCl}$ !], to be used again. This proposal, which the high price and inevitable loss of boric acid makes appear chimerical, was patented by Margueritte in 1855 (No. 159).

Garroway (No. 17395, 1889) patents this process once more; he hopes to improve the reaction by adding nitre-cake and employing a current of steam.

#### *By Hydrogen Fluoride.*

Weldon's patent No. 628, 1866, prescribes decomposition of  $\text{NaCl}$  by  $\text{HFl}$  into  $\text{NaFl}$ , boiling this with  $\text{MgO}$ , and decomposing the  $\text{MgFl}_2$  by  $\text{SO}_4\text{H}_2$ .  $\text{NaFl}$  may also be decomposed by  $\text{CaO}$ ,  $\text{CaCO}_3$ , or steam. The details will be given further on, when treating of the employment of  $\text{HFl}$  with sulphate.  $\text{NaCl}$  (according to him) can only be partly decomposed, if precipitated from a saturated solution by aqueous  $\text{HFl}$ , but much more completely if cooled  $\text{HFl}$  gas is passed in a moderately quick current into  $\text{NaCl}$  solution. Spilsbury and Maugham had already, in 1837, proposed the use of  $\text{HFl}$  (see below).

The proposal of Krantz (Germ. 65576) is intimately connected with his process for employing hydrofluosilicic acid, and will be described further on (p. 192).

Brochon (French pat. 208754) prepares  $\text{HFl}$  by the action of steam on fluorspar in a reverberatory furnace, and makes it act on  $\text{NaCl}$  in the fused state or in solution.

#### *By Hydrofluosilicic Acid.*

Spilsbury and Maugham in 1837 (No. 7277) patented the following process:—A solution of common salt is mixed with hydrofluoric, or, better, with hydrofluosilicic acid, and the precipitate of  $\text{Na}_2\text{SiFl}_6$ , by boiling with milk of lime, converted into  $\text{NaOH}$  and  $\text{CaSiFl}_6$ . Anthon tried this process in 1840 and obtained good results (Wagner's Jahresb. 1863, p. 228); but the difficulty of washing such a voluminous precipitate was not taken into account. A similar process was patented on March 2nd, 1858, by Newton for Le Chatelier, and in 1858 by Kessler in France. Hydrofluosilicic acid is prepared by melting a mixture of sand, clay, and fluorspar and condensing the vapours; this is employed for decomposing a solution of common salt. The precipitated  $\text{Na}_2\text{SiFl}_6$  is decomposed by ignition into  $\text{NaFl}$ , and this, by boiling



with chalk, into  $\text{Na}_2\text{CO}_3$  and  $\text{CaFl}_2$ . The latter is mixed with the  $\text{HCl}$  and gelatinous silica formed in the previous stages of the process, also with common salt; thus again  $\text{Na}_2\text{SiFl}_6$  is formed, and so forth (Hofmann, 'Report by the Juries,' 1863, p. 30).

Whether this process could ever pay, would depend to a great extent on the cheap production of hydrofluosilicic acid. In 1865 E. Karcher and Tessié du Motay patented in France the production of that acid (or, in the first instance, of  $\text{SiFl}_4$ ) by igniting a mixture of sand, fluorspar, and coal. (Former trials in that direction by Bredberg and Berthier are mentioned in Wagner's 'Regesten,' p. 20.) Fluorspar (Biedermann, in Hofmann's 'Bericht,' 1873, i. p. 316), silica, and clay were mixed in such proportions that a good slag could be formed and moulded with addition of coal into bricks, which were dried and smelted with coke in a blast-furnace of 33 to 40 feet height. The slag contained calcium silicates and still 15 to 20 per cent.  $\text{CaFl}_2$ . The gases given off, consisting of  $\text{SiFl}_4$ ,  $\text{N}$ ,  $\text{CO}$ , and  $\text{CO}_2$ , were collected at the mouth, and carried to five large wooden condensing-vessels in which slanting glass plates were placed and constantly kept wet. At the bottom of the vessels silica was deposited, and a solution of  $\text{H}_2\text{SiFl}_6$  was formed; the latter was methodically conducted from one of the condensers to another. An agitator, causing a finely divided spray of water, would probably replace the glass plates with advantage. It is not easy to produce acid beyond 1.072 sp. gr.=9 per cent.  $\text{H}_2\text{SiFl}_6$ ; for technical purposes half that strength would suffice. The latter costs at least 2 francs per kilog.; 100 litres of it are equivalent to 9 kilog. chamber-acid (of vitrol-chambers).

A factory, working by this plan and managed by F. Bothe, existed till 1870 at Grossblittersdorf near Saargemünd, but was not started again after the war, because several serious drawbacks had appeared. The decomposition of  $\text{SiFl}_4$  by water was not perfect; a good deal of it escaped and caused complaints on account of nuisance. In spite of an excess of silica,  $\text{HFl}$  was always formed as well, and caused great trouble in decomposing the salt. Worst of all was the fact that sodium fluosilicate is only very imperfectly decomposed into silicium fluoride and sodium fluoride by ignition, even after twenty-four hours' most intense heating, both with compressed and exhausted air. For these reasons the process was discontinued.

Lefranc and Vivien (French pat. 208878) give prescriptions for

manufacturing hydrofluosilicic acid which present no special interest.

This process has been taken up in a somewhat modified form by Krantz (Germ. pat. 65576 and 65784). He heats 1 part sodium fluosilicate with 2 sulphuric acid, spec. grav. 1.70, in a lead-coated boiler with false bottom, serving as a steam-bath. Sodium bisulphate is formed; the gases, consisting of hydrogen fluoride and silicon fluoride, are conducted in leaden pipes to two series of leaden Woulfe's bottles, half-filled with water and kept cool. Each bottle has near the bottom a neck, connected by means of gutta-percha tubing with a main pipe, communicating with a water-tank placed at a higher elevation. The gaseous current can be made to travel either in one or in the other direction. From these leaden receivers the gas is conducted into a series of similar glass receivers, and then into leaden chambers about 6 feet high, where dry calcium fluoride is spread in layers, 2 inches deep, on leaden shelves. The gas enters near the top and issues near the bottom. The water contained in the bottles absorbs first the whole of the gases, but later only the  $\text{HFl}$ ; while the  $\text{SiFl}_4$ , previously absorbed, is mostly driven out again and retained in the following bottles, where it is decomposed into silica and hydrofluosilicic acid, until here also the  $\text{HFl}$  again converts the  $\text{SiO}_2$  into silicon fluoside:  $\text{SiO}_2 + 4\text{HFl} = \text{SiFl}_4 + 2\text{H}_2\text{O}$ . This reaction can be followed up in the glass receivers, and the gaseous current through the leaden receivers must then be reversed. The gas arriving in the lead chambers is pure  $\text{SiFl}_4$ , which with the  $\text{CaFl}_2$  yields soluble calcium fluosilicate,  $\text{CaSiFl}_6$ . If the charge of any lead chamber has thus been completely transformed, it is put out of series, discharged, charged with fresh  $\text{CaFl}_2$ , and put into series as the last of the lot. The calcium fluosilicate is then transformed by sodium chloride into a solution of calcium chloride and a precipitate of sodium fluosilicate, which is employed again for the first stage of the process.

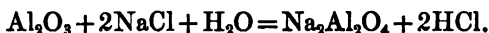
The hydrofluoric acid obtained in the leaden receivers is mixed with the sodium bisulphate previously obtained, a precipitate of sodium fluoride is formed with supernatant sulphuric acid, which is freed from  $\text{HFl}$  by a further addition of  $\text{NaHSO}_4$ ; it is then concentrated to spec. grav. 1.70 and again used for decomposing sodium fluosilicate. The sodium fluoride is then employed for preparing caustic soda, &c. The patent describes some further

modifications, for which I refer to the original, as they do not seem to be worth repeating here.

Reich (French pat. 233075) heats sodium fluosilicate with silica, to produce sodium silicate and  $\text{SiFl}_4$ ; the latter is reconverted into  $\text{H}_4\text{SiFl}_4$ , and the sodium silicate is decomposed by  $\text{CO}_2$ . The hydrofluosilic acid may be replaced by hydrofluoboric acid, and the silica by alumina.

*By Alumina.*

Tilghman in 1847 (No. 11556), patented, among other things, a process for making soda from common salt (or sulphate) by the assistance of alumina. The latter, made by heating aluminium sulphate, was to be filled in pieces of about  $\frac{1}{4}$  cwt. each into a red-hot cylinder of fireclay with a magnesia lining, and vapours of common salt mixed with steam passed into it. The latter are obtained by admitting steam into a cast-iron retort in which common salt is kept in igneous fusion. The reaction takes place thus :—



(We employ this formula for sodium aluminate merely for the sake of simplicity; probably different compounds, up to  $\text{Na}_6\text{Al}_2\text{O}_6$ , are formed.) Besides, strongly superheated steam is directly admitted into the apparatus, which must be strongly red hot or white hot. By a test-hole in the exit-pipe the quantity of steam is controlled; there ought to be little salt and much acid found in the gases. On the one hand,  $\text{HCl}$  is formed, and condensed by suitable apparatus; on the other hand, a mass containing sodium aluminate remains behind in the retort. This is lixiviated with hot water, the residue dried and used over again; the solution is treated with  $\text{CO}_2$ , by which aluminium hydrate is precipitated, whilst sodium carbonate remains in solution and can be obtained by crystallizing, &c. (exactly as in the manufacture of soda from cryolite, Chapter X.). When the process was carried out at Glasgow on a large scale, the impracticability of introducing common salt in this way must have become apparent; for there a paste was made from alumina and salt, formed into small hollow cylinders of 4 inches length and 1 or 2 inches diameter, dried sharply, and the decomposing-cylinder filled with them. They were finally got back without change of form, containing *partly* sodium aluminate, and were moistened with water and exposed to a current of  $\text{CO}_2$  and steam. On lixi-

viating, soda was obtained and alumina remained behind. Knapp (Liebig's Jahresb. 1847-48, p. 1052) states that the reaction of  $\text{Al}_2\text{O}_3$  on  $\text{NaCl}$  at a red heat is not very energetic; and the necessity of employing a white heat is very troublesome in practice. In Glasgow, in fact, only 32 per cent. of soda was obtained, and great difficulties were experienced in treating and recovering the light flocculent alumina—a difficulty attaching to all soda-making processes which employ alumina or silica. These facts, no doubt, were soon recognized after the publication of the process (which had awakened much interest); for the matter was laid aside till a cheaper and handier source of alumina was found in *bauxite*, a natural aluminium hydrate containing ferric oxide. Lechatellier and Jacquemart were the first who employed this mineral for preparing sodium aluminate, in the aluminium-works at Nanterre near Paris, and later on at Salindres (in 1861 and 1862), by mixing it with common salt and passing steam into the mixture in a closed vessel, or, better, in a reverberatory furnace at a high temperature. In what way the volatilization of the salt was prevented and the  $\text{HCl}$  condensed has not become known; but it is a fact that the aluminate sent into the trade by Morin was not made from common salt but from sulphate. In 1862 (No. 2050) Gossage again patented a process, similar to Tilghman's but employing a peculiar furnace, which has been described when mentioning the silica process, proposed at the same time and preferred by himself. A similar process is that of Hargreaves (No. 2121, 1867). In 1874 (No. 2639) Grüneberg and Vorster took out an English patent upon the same subject. Common salt and alumina are made into a paste; the mass is dried, broken into small pieces, and treated with red-hot steam.  $\text{HCl}$  escapes, and  $\text{Na}_2\text{Al}_2\text{O}_4$  remains behind. The latter is dissolved out from the impurities, and decomposed either by  $\text{CO}_2$  or by  $\text{CaO}$ , according to whether carbonate or caustic soda are to be obtained. Instead of alumina, ferric oxide or any other metallic oxide may be employed (?). This process was actually tried, but had to be discontinued because the vessels would not stand—the same drawback which has occurred in so many theoretically sound processes.

Anderson (Engl. pat. 2801, 1867) passes superheated steam first over alkaline chlorides, which are thereby volatilized, and then over clay, to form alkaline silicate and aluminate.

Lieber (Engl. pat. 2183 and 4580, 1887) heats alkaline chlorides with sulphate of alumina in a current of superheated steam; at first HCl, afterwards  $\text{SO}_2 + \text{O}$  escapes, and alkaline aluminate remains behind.

*With Alumina, after converting the Sodium Chloride into Sulphate.*

C. F. Claus (Engl. pat. 4311, 1891) mixes hydrated alumina, either in the shape of bauxite or recovered in the process, with its weight of sodium chloride, and moulds the mixture with water into balls or bricks which are dried; then by a hot mixture of steam, air, and  $\text{SO}_2$ , the NaCl is converted into sodium sulphate, at such a temperature that the chemically combined water is not split off from the alumina, but high enough to prevent the formation of aluminium sulphate. The presence of alumina facilitates the reaction, by preventing the mass from fusing. If less aluminium hydrate has been employed than is necessary for completing the formation of aluminate, much alkaline sulphide is formed, which may be afterwards converted into carbonate by gases containing  $\text{CO}_2$ . In this case the object is not so much to form alkaline aluminate as to remove the difficulties otherwise militating against the manufacture of sodium sulphide.

The transformation of the chloride into sulphate takes place in a series of furnaces or brick chambers, or brick-lined iron vessels, connected, as in a Hargreaves apparatus (Vol. II. p. 258), in such a manner that the gaseous current can be directed in any given way and that any chamber may be put out of turn. The chambers are charged with the salt-alumina balls, and are systematically heated with pyrites-kiln gases, as minutely described in the patent; this part entirely agrees with the Hargreaves process.

When the charge has been completely transformed into sulphate, it is taken out of the chambers and is put into a second set of chambers, arranged and manipulated exactly like the first. The gas here employed is carbon monoxide, hydrogen, water-gas or the so-called semi-water gas, and by this the sulphate is at first reduced to sulphide. This is later on decomposed by the water chemically combined with the alumina, and yields up the sulphur as  $\text{H}_2\text{S}$ ; the alkali with the alumina forms sodium aluminate. If the heat conveyed by the gases from the producer is not sufficient,

heated air is passed in, in order to raise the temperature by burning part of the gas.

The novelty, in this case especially, consists in reducing the  $\text{Na}_2\text{SO}_4$  to  $\text{Na}_2\text{S}$  by reducing gases alone, without any addition of carbon. The gases mixed with  $\text{H}_2\text{S}$  are then worked for sulphur by the well-known process due to the same inventor (Vol. II. p. 895).

Instead of two separate sets of chambers a single set of double length may be employed; this is arranged in such manner that part of it can be treated with pyrites-kiln gases and part with water-gas. This arrangement, minutely described in the patent, avoids moving the sulphate before reducing it to sulphide.

The sodium aluminate, or mixture of such with sodium sulphide, remaining behind is dissolved in hot water, and is converted into sodium carbonate and aluminium hydrate by gases containing  $\text{CO}_2$ . In the presence of sulphide the gases must at first go into the sulphur-recovery apparatus. This process is also applicable to sodium sulphate obtained by any other process, which is mixed with hydrated alumina and treated as above.

Kayser, Williams, and Young (Engl. pat. 11492, 1887) mould a mixture of salt and clay (not alumina!) with water into bricks, which are dried, and are heated in a cupola with hot gases and superheated steam. The clay acts upon the  $\text{NaCl}$  and drives off  $\text{HCl}$ , long before a visible red heat has been attained; the action quickly increases as the temperature rises, and is finished after heating to a red heat for 24 hours. The residue is an "acid silico-sodium aluminate," which in the case of a proper mixture contains 33 per cent.  $\text{Na}_2\text{O}$ ; it is then insoluble in water and infusible even at incipient white heat. It is crushed, and is fused with sufficient soda to bring up the percentage of  $\text{Na}_2\text{O}$  to 50 per cent. This "basic silico-sodium aluminate" is deliquescent; on lixiviation it yields a solution containing from 80 to 90 per cent. of the total  $\text{Na}_2\text{O}$  as hydrate, the remainder as carbonate and aluminate. The insoluble residue contains recovered aluminium silicate, free from iron, which is employed instead of fresh clay for the first reaction. The best description of clay for this purpose is that containing  $2\text{SiO}_2$  to  $1\text{Al}_2\text{O}_3$ , and this is obtained by adding sand to ordinary clay, or removing an excess of sand from clay. The fire-gases entering the cupola must contain enough steam to form  $\text{HCl}$  with the chlorine, and enough oxygen

to avoid the formation of CO and its reducing action. The patent specification (printed in Journ. Soc. Chem. Ind. 1887, p. 730) contains a diagram of the gas-producer and of the cupola (the "converter"), to which I must refer, as the process has evidently not turned out to be practicable. A number of further details are described in another patent of the Kayser Patent Co. (Engl. pat. 10202, 1891; Journ. Soc. Chem. Ind. 1892, p. 36), which makes the impression as if the process had been actually tried on the large scale, but probably without much success.

*By Kieserite and Alumina.*

Lieber (Germ. pat. No. 9610, 1878) proposes mixing alkaline chlorides with magnesium sulphate (occurring at Stassfurt as kieselite) and as much crude alumina (in the state of bauxite &c.) as will decompose the alkaline sulphates formed. The mixture is moulded into bricks, which are dried and heated to a red heat in a kiln, steam being passed through at the same time. First there are formed alkaline sulphates and hydrochloric acid. The latter is condensed in the usual manner; the sulphates are acted upon by the alumina, sulphur dioxide and alkaline aluminate being formed. The ignited mass is lixiviated with water and treated with carbon dioxide, so that alkaline carbonate and a precipitate of aluminium hydroxide are obtained. Instead of HCl, chlorine may be obtained by submitting the dried mass at  $900^{\circ}$  to a gentle current of air, previous to igniting it in the kiln.

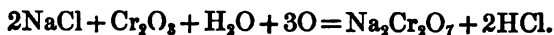
[This process is quite impracticable, as the  $\text{SO}_2$  would escape together with the fire-gases.]

*By Aluminium Chloride.*

Swager (Monit. Scientif. 1868, p. 838) proposes to mix a solution of NaCl and of  $\text{Al}_2\text{Cl}_6$ ; the double salt,  $2\text{NaCl}, \text{Al}_2\text{Cl}_6$ , is obtained by drying, and blown by means of a fan-blast, in the form of a fine powder, through a red-hot retort in which it is exposed to superheated steam. Sodium aluminate and HCl are generated; the former is decomposed by  $\text{CO}_2$  into  $\text{Na}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , which is again converted into  $\text{Al}_2\text{Cl}_6$ .

*By Chromium Oxide and Steam.*

Kessler, in 1867, patented in France the following process:—Sodium (or potassium) chloride is intimately mixed with chromium sesquioxide, alone or along with manganese, or with chrome iron-ore or lead chromate, and in a red-hot state treated with superheated steam. With the assistance of atmospheric oxygen, sodium bichromate and hydrochloric acid are formed—



When the reaction is finished and the mass cooled down, it is mixed with coal and again heated to a dark-red heat. Now sodium carbonate and chromium oxide are formed, CO or CO<sub>2</sub> being given off—



or



The sodium carbonate is dissolved out, and the residue Cr<sub>2</sub>O<sub>3</sub> used for decomposing fresh salt. This proposal is impracticable, because the reaction between Cr<sub>2</sub>O<sub>3</sub>, NaCl, and superheated steam (already patented by Swindells in 1851) is very incomplete.

Rather different are the patents of Hargreaves and Robinson (Nos. 508 and 509, 1872). The alkaline chromates, obtained in the chlorine process patented by the same inventors, are to be reduced by hydrogen, carbonic oxide, or hydrocarbons; in the first case the hydrates, in the latter cases the carbonates of the alkalis are obtained. Or the chromates are reduced by heating with finely divided coal (as in Kessler's process), and cooled in closed vessels, to prevent the re-formation of chromates.

Gattman's patent (No. 1184, 1868) is very similar to the above. He mentions that ferric chloride volatilizes, and that sodium nitrate or manganese oxide must be added.

*By Oxalic Acid.*

Kobell (Wagner's 'Regesten,' p. 18) proved that sodium chloride can be converted into carbonate by oxalic acid on ignition, CO and HCl escaping. But, looking at the high price of oxalic acid, only those processes can claim a technical interest which recover that acid. All endeavours in this direction are founded upon the slight solubility of acid sodium oxalate in water, and are carried

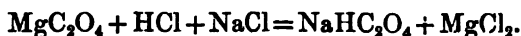


out by adding to a concentrated solution of salt an excess of oxalic acid, so that the acid oxalate,  $C_2HNaO_4 + H_2O$ , is precipitated and HCl remains in solution. The precipitate is converted into caustic soda and calcium oxalate by boiling with milk of lime, and the oxalic acid recovered from the latter by sulphuric acid. This process was patented by Samuel, No. 7873, 1838, again by Margueritte, No. 159, 1855, and by Weldon, No. 629, 1866, but with the addition that the hydrosodic oxalate was to be boiled with quicklime or calcium carbonate. The latter does not answer the purpose, as Anthon and R. Wagner have found ('Regesten,' p. 18). Only half of the oxalic acid is precipitated by  $CaCO_3$ , the other half remaining dissolved as  $C_2Na_2O_4$ ; but a mixture of milk of lime and chalk, or the latter by itself (as proposed by Samuel) fulfils the intention. The process is not practicable, because much oxalic acid is lost, its recovery is not easy, and its price is high. As No. 2864, 1864, Newton (for Bang) patented the decomposition of NaCl with *ammonium oxalate* in hot concentrated solutions;  $NH_4Cl$  remains dissolved,  $NaHC_2O_4$  falls down, is isolated by decantation, washed with a cold concentrated solution of pure  $NaHC_2O_4$ , decomposed by CaO into NaOH and  $CaC_2O_4$ , and the latter converted by  $NH_3$  (from the  $NH_4Cl$ ) and  $CO_2$  into  $CaCO_3$  and  $(NH_4)_2C_2O_4$ . (This patent did not get beyond the stage of provisional protection.) Knab obtained a French patent (Jan. 3, 1877) for exactly the same process.

Marchand (French pat. 213354) again causes a concentrated solution of oxalic acid to act on the NaCl, thus expelling HCl; the sodium oxalate is to be transformed by lime into caustic soda and calcium oxalate, and from the latter the oxalic acid is to be recovered by sulphuric acid.

#### *By Magnesium Oxalate.*

Bohlig (Dingl. Journ. ccxiv. p. 621), 1st, mixes magnesium oxalate, common salt, and hydrochloric acid cold, and lets the mixture stand. A crystalline precipitate of  $NaHC_2O_4$  and a sirupy solution of  $MgCl_2$  are obtained, according to the equation



The solution of  $MgCl_2$  is displaced by water; and as it contains an excess of HCl, it is used over again till it is saturated. 2nd. The

$\text{NaHC}_2\text{O}_4$ , by agitation with  $\text{MgCO}_3$  and water at a pressure of two atmospheres, is converted into a coarse crystalline precipitate of  $\text{MgC}_2\text{O}_4$  and a concentrated solution of  $\text{NaHCO}_3$ . 3rd. The latter, by boiling with magnesia, is converted into a solution of  $\text{Na}_2\text{CO}_3$  and  $\text{MgCO}_3$ . Thus one half of the  $\text{MgCO}_3$  required in the second stage is obtained; the second half is obtained by treating the  $\text{MgO}$  formed in the 4th stage with fire-gases. The solution of soda contains a little sodium oxalate, which on concentration to  $77^\circ \text{B}$ . and cooling is completely precipitated. 4th. The solution of  $\text{MgCl}_2$  is boiled down, and by heating decomposed into  $\text{MgO}$  and  $\text{HCl}$ . 5th. The oxalic acid intended for replacing that which has been lost is prepared by heating caustic potash with sawdust to dryness, melting, lixiviating, recrystallizing the potassium oxalate, and precipitating  $\text{MgC}_2\text{O}_4$  by means of  $\text{MgCl}_2$  or  $\text{MgSO}_4$ . Pure oxalic acid can be obtained by treating the magnesium oxalate with  $\text{HCl}$ . The principal weak points of this rather ingeniously combined proposal seem to be, 1st, the difficulty of completely decomposing the  $\text{MgCl}_2$ , and, 2nd, the expense of replacing the oxalic acid lost.

#### *By Calcium Sulphide.*

According to Greenshield's patent (No. 1136, 1852), gypsum and small coal are to be brought to a red heat and common salt and more small coal added, and heat applied till no more gas is given off; the mass is cooled and lixiviated, the solution boiled down; and the salt obtained is fused in a black-ash furnace with coal and chalk. The description of the process is very obscure, but does not invite any special study.

#### *By Ferrous Sulphide.*

Raynaud (Engl. pat. 14483, 1890) heats common salt with ferrous sulphide in contact with air; chlorine escapes, and a mixture of sodium sulphide and ferric oxide remains behind. This is mixed with coal and fused, thus forming ferro-sodium sulphide, from which by means of  $\text{CO}_2$  sodium carbonate and  $\text{FeS}$  are obtained, the latter to be used over again. [The first part of this process is simply taken from Longmaid, Vol. II. p. 128, the second from Blythe and Kopp, *vide infra*, neither of which processes has been practically successful.]

## CHAPTER XII.

MANUFACTURE OF SODA FROM SODIUM SULPHATE  
WITHOUT PREVIOUS REDUCTION TO SULPHIDE.*By Potassium Carbonate.*

(Wagner's 'Regesten,' p. 45.)

C. F. HAGEN showed, in 1768, that from a mixed solution of sodium sulphate and potassium carbonate first a crop of potassium sulphate, and then one of sodium carbonate is obtained. Bergman (1781), Wiegleb, Göttling, Accum, and Nasse have each described this process, which, at the then ruling prices of potash and soda, was not so completely absurd in an economical point of view as in 1840, when Anthon thought it worth while to try it on a large scale and pronounced favourably upon it!

*By Caustic Lime.*

Already in 1789 Delius intended decomposing sulphate by lime into caustic soda and gypsum; afterwards Achar, Scheele, Klaproth, Götting, and Westrumb occupied themselves with the same matter, and, indeed, made soda by this process. Anthon in 1840 showed that the decomposition is only imperfect (Wagner's 'Regesten,' p. 46). Claussen in 1852 took out an English patent (No. 13956) for manufacturing sodium hydrate and carbonate by boiling sodium sulphate with the hydrate of calcium, barium, or strontium: the earthy sulphate is precipitated; the NaOH remains in solution; by long exposure to the air it is changed into carbonate. Common salt is also decomposed "by means of certain organic acids, which are afterwards decomposed by heat," by "gaseous acids," by "hydrates, oxides, peroxides, and certain metallic bases; also by certain carbonates, carbonate of ammonia excepted." From this medley everybody may pick out what suits him. A better result than by boiling with quicklime under ordinary circumstances was expected to be attained by Hunter

(patent No. 1011, 1865) by boiling under pressure. Good results were to be obtained with sulphate of soda "by boiling a solution of sp. gr. 1.100, at pressure of from 40 to 50 lbs. per square inch," and with sulphate of potash "by boiling a solution of sp. gr. 1.100, at a pressure of from 80 to 90 lbs. per square inch, till a test shows that the reaction is finished. An excess of lime is useful, and may be utilized by employing the residue of  $\text{Ca(OH)}_2$  and  $\text{CaSO}_4$  for the first treatment of a fresh portion of alkaline sulphates, and decomposing the latter by a second boiling with fresh quicklime. Some varieties of lime are less active than others. The gypsum is separated from the caustic lye by filtering under pressure, lest any backward decomposition set in; and the caustic soda is used as such or converted into carbonate by introducing  $\text{CO}_2$  or by evaporating over  $\text{CaCO}_3$ ." Hill (Chem. News, xxvii. p. 165) examined the action of lime on sulphate with or without pressure, and obtained very discouraging results. By boiling without pressure he could only obtain 1 per cent. of the sulphate as  $\text{NaOH}$ ; at a pressure of nearly 3 atmospheres, only 6 per cent., and at a pressure of 13 atmospheres, continued for several hours, only 13 per cent. was converted into  $\text{NaOH}$ .

Tessié du Moray once more patented this process (French pat. 92312, 1871), with the assertion that at a pressure of from 2 to 20 atmospheres 75 or 80 per cent. of the sulphate can be decomposed. In experiments made in my laboratory by Reisz (Dingl. Journ. ccxxxviii. p. 69) at a pressure of 5 atmospheres a totally insufficient decomposition was obtained, just as in Hill's experiments. At ordinary temperatures a mixture of 1 mol.  $\text{Na}_2\text{SO}_4$  + 1 mol.  $\text{CaO}$ , dissolved in 15 times its weight of water, was decomposed only to the extent of 6.55 per cent.; in the presence of 180 parts of water to 1 of  $\text{Na}_2\text{SO}_4$  the decomposition amounted to 28.8 per cent. At a higher pressure (5 atmospheres) the decomposition in the presence of 6 parts of water amounted to 3.1 per cent., with 10 water to 11.2 per cent., with 25 water to 31.7 per cent.

Bevan and Cross (Dingl. Journ. ccxlii. p. 137) obtained very similar results.

#### *By Caustic Baryta.*

Undoubtedly the decomposition of sodium sulphate and barium hydrate to barium sulphate and sodium hydrate, which takes place even in cold solutions directly and completely, would be an

extremely convenient soda-making process, if the preparation of caustic baryta were possible in a simple and cheap way.

Patents for this process have been granted :—to Fuller (No. 4357, 1819), who intended making caustic baryta by heating carbonate, and utilizing the  $\text{CO}_2$  driven off by carbonating the caustic soda ; further, to Samuel (No. 7873, 1838), who employed the sulphides of barium and strontium, made from the sulphates by reduction with coal, and converted the sodium sulphide formed into carbonate by means of  $\text{CO}_2$  ; moreover he patented the direct application of barium or strontium hydrate, made from the sulphides by means of copper oxide. Anthon in 1840 tried Samuel's process, and obtained good results.

R. Wagner ('Regesten,' p. 50) also found that sodium sulphate is easily and completely decomposed by caustic baryta at all temperatures and pressures, and that, as H. Rose had stated, a solution of sodium hydrate, if  $\text{CO}_2$  is kept off, does not act upon  $\text{BaSO}_4$ . Hofacker (Dingl. Journ. clxix. p. 76) made again the "novel" proposal of employing caustic baryta, obtained by calcining the native carbonate or by reducing the sulphate and treating the  $\text{BaS}$  with  $\text{CuO}$ , for decomposing sodium sulphide ; Hunter, No. 2876, 1864, and Lyttle, No. 455, 1875, patented the same thing.

All these proposals must remain futile until a much cheaper process for making caustic baryta than any of those known hitherto has been discovered. When this is done, then certainly, as Hofmann says (Report by the Juries, 1863, p. 64), the alkali-manufacture will be revolutionized. Hofmann adds that in such a case the use of caustic baryta would mostly supersede that of caustic alkaline lyes.

Dr. Angus Smith (Inspectors' Report, 1877-78, p. 34) believed that caustic baryta can be cheaply made by the process described there—viz., adding a little  $\text{MnO}_2$  to a solution of  $\text{BaS}$  and passing a current of air through it. A precipitate of sulphur and a solution of barium hydrate are formed, while  $\text{MnO}_2$  only acts as a carrier of oxygen and remains as before.

His soda-ash process might be formulated thus :—

1.  $\text{BaSO}_4 + 2\text{C} = \text{BaS} + 2\text{CO}_2$  ;
2.  $\text{BaS} + \text{MnO}_2 + \text{H}_2\text{O} = \text{Ba}(\text{OH})_2 + \text{MnS} + \text{O}$  ;
3.  $\text{MnS} + 2\text{O} = \text{MnO}_2 + \text{S}$  ;
4.  $\text{Ba}(\text{OH})_2 + \text{Na}_2\text{SO}_4 = 2\text{NaOH} + \text{BaSO}_4$ .

But, unfortunately, the above reaction takes place only in dilute liquids ; moreover barium hyposulphite is also always formed ; and these circumstances, combined with the expense of reducing the  $\text{BaSO}_4$  and lixiviating the  $\text{BaS}$ , would perhaps make the process not economical. But it is certainly worthy of the attention of practical men.

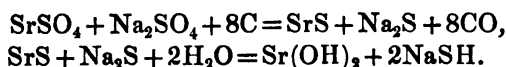
*By Caustic Strontia.*

(Compare also Potassium Carbonate and Caustic Lime, p. 201.)

Ungerer (Dingl. Journ. clxxxviii. p. 140) makes the following proposal :—First, by boiling equivalent quantities of ammonium sulphate and sodium chloride in concentrated solutions, anhydrous sodium sulphate is to be obtained, which is precipitated and fished out ; on cooling, ammonium chloride crystallizes ; and the mother liquor on evaporation again furnishes sodium sulphate. The latter, dissolved in water and mixed with caustic strontia, yields very pure caustic soda and a precipitate of strontium sulphate. The ammonium chloride previously obtained is converted by calcium carbonate into ammonium carbonate ; and this, digested with the strontium sulphate, yields strontium carbonate and ammonium sulphate. The latter serves for decomposing fresh salt ; the former is mixed with coal and ignited in a reverberatory furnace with the assistance of steam, till it has given up its carbonic acid, which is easily done. Thus the raw materials are only common salt and lime and as much strontia [and ammonia !] as is required for replacing the inevitable loss in manufacturing. The hydrochloric acid is certainly lost with the calcium chloride. Ungerer points out as advantages of his process that strontium sulphate can be converted into carbonate by digestion with ammonium carbonate, and that strontium carbonate more easily yields up its  $\text{CO}_2$  than  $\text{BaCO}_3$ . But he himself admits that the decomposition of  $\text{SrSO}_4$  is not perfect ; strontium sulphide is formed, and consequently sodium sulphide, and that in considerable quantity. Even apart from that, this ingeniously combined process is useless ; a considerable quantity of  $\text{SrCO}_3$  will not be changed into  $\text{SrO}$ , and will consequently be lost ; and the loss of ammonia will be even worse. If ammonia is to be employed at all, no doubt the much simpler process of Dyar and Hemming will be resorted to.

Gray (Amer. pat. 459688) treats alkaline sulphates with strontium hydrate, converts the strontium sulphate formed by  $\text{MgCO}_3$  into strontium carbonate, and recovers the caustic strontia from the latter by heating in an atmosphere of steam.

Eichstädt (Engl. pat. 15136, 1891) describes a new form of the strontia process. Equivalent proportions of strontium sulphate and sodium sulphate are heated with a quarter of their weight of coal; the melted mass is dissolved in water. The following reactions take place:—



On cooling the strontium hydrate crystallizes out and is utilized for preparing caustic soda from sodium sulphate. The sodium sulphhydrate remaining in the mother liquor can be utilized in various well-known ways.

#### *By Calcium Bicarbonate.*

Pongowski (French patent of March 27th, 1872) adds to a solution of alkaline sulphate a little more than the theoretical quantity of finely powdered limestone, covers up the vessel, and conducts a current of  $\text{CO}_2$  into it, constantly agitating. Calcium bicarbonate is formed, which is decomposed with the alkaline sulphate; after eight hours the latter is completely converted into carbonate. The mixture is allowed to settle, the liquid poured off from the precipitate and boiled down.

Hilgard (Ber. deutsch. chem. Ges. 1892, p. 3624) states that the above reaction was first proposed by Alex. Müller, of Stockholm, in 1859. He himself carried it out with potassium and sodium sulphate, and therefrom deduced the formation of "natural soda" (Vol. II. p. 58); but it occurs to any considerable extent only in extremely dilute solutions, and, on evaporation, the alkaline carbonates formed are almost entirely reconverted into sulphates by the  $\text{CaSO}_4$ . The process is entirely useless for the alkali manufacture, and Pongowski's statements are quite erroneous, as I have already stated in Dingl. Journ. ccxliii. p. 157.

#### *By Strontium Carbonate.*

Most of the proposals made for barium carbonate also refer to this.

*By Barium Carbonate.*

According to Wagner's 'Regesten,' p. 46, the first experiments with this were made in 1826 by Kastner at Erlangen, and that in the dry way, but unsuccessfully; Anthon, on repeating, in 1840, Kastner's experiments, was no more fortunate. Kölreuter first tried the wet way, in 1828. He prescribed the precipitation of barium carbonate from a solution of chloride by means of ammonium carbonate, washing out the precipitate, putting it in the state of paste into a solution of sodium sulphate, and boiling for an hour with the latter. One part of  $\text{BaCO}_3$  (calculated as dry) is to decompose two parts of crystallized sodium sulphate, and to yield  $1\frac{1}{2}$  part of soda crystals. But it is a fact that in this way, even with an excess of  $\text{BaCO}_3$  and on boiling,  $\text{Na}_2\text{SO}_4$  can never be completely decomposed. This was confirmed in 1832 by Erdmann and Buchner. C. Lennig in 1851 received a patent in several German States for a process of making soda from sulphate by means of barium carbonate. In England (No. 976, 1856) Balmain and Colby again patented the reaction between  $\text{BaCO}_3$  and the alkaline sulphates, without any essential innovation. In 1858 Kessler again drew attention to barium carbonate; also Hofacker, who started from the erroneous supposition that  $\text{BaCO}_3$  and  $\text{Na}_2\text{SO}_4$  are smoothly and easily converted into  $\text{Na}_2\text{CO}_3$  and  $\text{BaSO}_4$ . But unfortunately a large portion of  $\text{Na}_2\text{SO}_4$  always remains undecomposed, at whatever temperature the operation may be conducted.

In Wagner's Jahresb. 1864, p. 165, the experiments of Rose and Malaguti in this direction are mentioned.

Spring (Bull. Soc. Chim. xlv. p. 299) found that by briskly agitating an intimate mixture of anhydrous sodium sulphate and dry barium carbonate 9.5 per cent.  $\text{BaSO}_4$  was formed. By a pressure of 6000 atmospheres 59 per cent. of  $\text{BaCO}_3$  was at once transformed into  $\text{BaSO}_4$ , and by grinding several times over and always pressing as before the transformation could be brought to 80.3 per cent in 14 days. Higher temperatures act in a direction contrary to the reaction. [Of course experiments at a pressure of 6000 atmospheres have no technical interest.]

As late as 1892 Nauhardt took a French patent (No. 223339) for manufacturing sodium carbonate by digesting sodium sulphate with barium carbonate, prepared from  $\text{BaS}$  by  $\text{CO}_2$ .



Dr. O. Schott (private communication) obtained, by melting barium carbonate and sodium sulphate at a strong heat, a fused product which yielded with water a strongly alkaline liquor and a residue of almost pure  $\text{BaSO}_4$ . The latter was in a coarsely crystalline state, which explains its not being reconverted on contact with the hot alkaline liquor. But as Schott had to employ an excess of sodium sulphate, his process would be useless from that cause alone; and it would certainly be more expensive than the treatment in the wet way with the aid of carbonic acid.

*By Barium Carbonate and Caustic Lime.*

This reaction was patented by Townsend (No. 3295, 1867).

Hill (Chem. News, xxvii. p. 165) mentions that on boiling equivalent quantities of sodium sulphate, barium carbonate, and lime under pressure (but what pressure?) a complete conversion into caustic soda had been attained, but he doubts the possibility of recovering the barium carbonate from the mixture of barium sulphate and calcium carbonate in an economical way.

V. Wartha (private communication) found this reaction to take place at the ordinary pressure. On testing it myself, I have found that on boiling a moderately dilute solution of sodium sulphate with  $1\frac{1}{2}$  equivalents of precipitated barium carbonate and caustic lime, the conversion into caustic soda was complete at the ordinary pressure. But this does not succeed with native barium carbonate, and the recovery of the  $\text{BaCO}_3$  from the  $\text{BaSO}_4$  would cause much expense (comp. below).

*By Barium Bicarbonate.*

An anonymous person obtained a patent, through H. Taylor, No. 13556, 1851. This patent refers to barium and strontium salts, and prescribes the regeneration of their carbonates from the sulphates by reduction to sulphides and application of  $\text{CO}_2$ ; the  $\text{H}_2\text{S}$  escaping is to be burnt into S and  $\text{H}_2\text{O}$ , or into  $\text{SO}_2$  for acid-chambers. He also mentions that the decomposition of the sulphates with barium or strontium carbonate is "facilitated" by a current of  $\text{CO}_2$ ; but he was evidently not acquainted with the *necessity* of this addition, nor does he give any special instructions

for carrying out the above-mentioned reactions, which are merely mentioned as suggestions.

Much better results are obtained by working with barium bicarbonate; in this case complete decomposition can be obtained with equivalent quantities of the two salts. In 1857 R. Wagner (*Jahresb.* 1857, p. 104) proved that a clear solution of barium bicarbonate, obtained by passing  $\text{CO}_2$  (no doubt in great excess) through  $\text{BaCO}_3$  suspended in water, decomposes with  $\text{Na}_2\text{SO}_4$  into  $\text{BaSO}_4$  and  $\text{NaHCO}_3$ ; but this process, considering the very slight solubility of barium bicarbonate (1 : 800 water), cannot lay claim to any technical value.

A further step was taken by Kuhlmann (*Hofmann, Report by the Juries*, 1863, p. 32), who, on repeating Wagner's experiments, got better results by employing a pressure of three or four atmospheres, simply because then a somewhat more concentrated solution of barium bicarbonate can be obtained. Very important was the remark made by Wagner in his '*Jahresbericht*,' 1864, p. 166, that complete conversion of  $\text{BaCO}_3$  into  $\text{BaH}_2(\text{CO}_3)_2$  is not necessary, and that a comparatively slight proportion of the latter may make the decomposition of  $\text{Na}_2\text{SO}_4$  perfect. For all that, the great dilution of the liquids prevented an industrial application of the process; and this was only approached by a proposal made by Brunner (*Dingl. Journ.* clxxvi. p. 127). It consisted in dissolving 1 part of sodium sulphate in 30 or 40 parts of water, suspending in it 2 parts of barium carbonate obtained by precipitation, and passing through the liquid at the ordinary temperature a current of carbonic acid, with frequent shaking or stirring. With a few grams of substance the decomposition was complete in an hour. The resulting solution contains, besides sodium bicarbonate, a little barium bicarbonate, which on boiling is decomposed into  $\text{CO}_2$  and precipitated  $\text{BaCO}_3$ . Of natural barium carbonate, finely ground, a large excess (about four times the quantity of sodium sulphate) is required. In order to prepare precipitated  $\text{BaCO}_3$ , which is more active, native sulphate of baryta was to be ignited with powdered coal and rosin in a crucible, the product lixiviated with water, and the solution treated with  $\text{CO}_2$ . Any barium sulphide remaining in the precipitate does no harm, as it is not decomposed afterwards. The carbonic acid for this process was to be prepared by means of limestone and hydrochloric acid (*sic*!); "but since the quantity of  $\text{HCl}$  obtained in decomposing the  $\text{NaCl}$

is not sufficient for supplying the quantity of  $\text{CO}_2$  required for this process, some more must be made in different ways, of which a sufficient number are known" (!). This statement plainly appears, in each sentence, to be based on mere experiment, with complete ignorance of the conditions required in practice. What should be done with the sulphuretted hydrogen is not even hinted at by Brunner.

I myself, unacquainted with either Taylor's patent or Brunner's proposal (the latter of which was only published after I had completed my own labour), but incited by Wagner's publications, independently hit upon the plan of making the process technically possible by not commencing with a solution of barium bicarbonate, but passing carbonic acid into a solution of sodium sulphate in which barium carbonate was suspended; the small quantity of barium bicarbonate formed would at once decompose sodium sulphate, and would be removed from the liquid as barium sulphate, thus enabling the liquid to dissolve a further quantity of barium bicarbonate, and so forth, till all the sodium sulphate was decomposed. But in order not to lose too much carbonic acid and to make the regeneration of barium carbonate feasible in an economical way, a combination of apparatus and processes was thought out, which is described in an English patent, No. 1108, 1866, and in the 'Chemical News,' xxvii. p. 139. Here we shall only mention the principal features very briefly. The  $\text{CO}_2$  is made by burning coke, or taken from a lime-kiln, or purified by Ozouf's plan (that is, first passing it through a solution of sodium carbonate, which allows the indifferent gases to escape, and on boiling gives off pure  $\text{CO}_2$ ). It then passes through several closed iron cylinders, provided with mechanical agitators, containing a solution of sodium sulphate along with a sufficient quantity of precipitated barium carbonate; when the decomposition is finished in the first cylinder, the gas is turned on to the second cylinder, whose contents are partially finished whilst the first cylinder is getting emptied and refilled, and then receives the gas issuing from the other cylinder. As, however, the current of  $\text{CO}_2$  must be a strong one and a good deal of it escapes even from the second cylinder, the gas is conducted through further vessels, in which it acts upon barium sulphide, and thus the  $\text{CO}_2$  is completely spent;  $\text{H}_2\text{S}$  escapes, mixed with indifferent gases; and  $\text{BaCO}_3$  is precipitated. The latter is at once utilized in the state of mud in the

first cylinder. The barium sulphide is obtained from the  $\text{BaSO}_4$  formed in the first vessels by igniting with coal and lixiviating, which with proper apparatus presents no difficulty. Up to this stage I had actually carried out the process on a rather large scale. For the most difficult part of my task, the utilization of the  $\text{H}_2\text{S}$ , I had in my patent made several proposals, which, however, were never practically tried, and which undoubtedly could not have been carried out exactly in the way proposed on any really large scale. In my publication I admit that my process would cost more for plant and working expenses than Leblanc's; but a much larger yield and much purer carbonate is obtained by it; and I thought it well adapted for making such pure alkali, provided that the difficulty of disposing of the sulphuretted hydrogen could be satisfactorily overcome. Now-a-days I should not consider my own proposal able to compete, even for pure alkali, with the ammonia process, which likewise supplies very pure soda.

Three years later Puissant patented something similar in France. He is silent on the recovery of  $\text{BaCO}_3$ ; and he suggests decomposing the solution of sodium bicarbonate with lead sulphate into sodium sulphate and lead carbonate, the latter to serve as white lead [which it cannot do]. This is properly only a white-lead process, and that an impracticable one. Lawrence Smith in 1873 ('Chemical News,' xxvii. p. 310) described the same process (with barium carbonate, carbonic acid, and sodium sulphate) as one never before described (!); he adds the proposal to prepare the alkaline carbonates by calcining the tartrates or oxalates, which can be obtained from barium carbonate, sodium sulphate, and the organic acid. Of course this could not be intended for a technical process at all.

Bramley (Engl. 1050, 1886) reverts to this process. He starts with  $\text{BaCl}_2$ , obtained by a very uneconomical process, viz. reducing  $\text{BaSO}_4$  by coal and decomposing the  $\text{BaS}$  by an excess of hydrochloric acid (!). This he converts into  $\text{BaCO}_3$  by treating the solution with  $\text{MgCO}_3$  and  $\text{CO}_2$  under pressure, heating and agitating till the excess of  $\text{CO}_2$  has been expelled. The solution of  $\text{MgCl}_2$  is separated from the  $\text{BaCO}_3$  precipitate, and is treated for the recovery of  $\text{MgO}$ ,  $\text{Cl}$ , and  $\text{HCl}$  (which is not yet economically possible). The washed  $\text{BaCO}_3$  is then decomposed with  $\text{Na}_2\text{SO}_4$  and  $\text{CO}_2$  in the way already described. The solution of

sodium bicarbonate formed is heated with MgO in a closed agitator, and thus sodium carbonate and magnesium carbonate are formed, the latter being used as before.

[The introduction of the magnesia into this process must make it more complicated and expensive, without offering a corresponding advantage.]

Baranoff (Engl. pat. No. 9555, 1895) improves the method by preparing barium sulphide from the sulphide with exactly the theoretical quantity of carbon (thus producing a practically complete reduction), grinding the crude barium sulphide, and directly introducing the powder into a solution of sodium sulphate, into which a stream of carbonic acid is immediately directed. By thus avoiding contact with air, very pure alkali is obtained.

*By Alumina as Bauxite and by Ferric Oxide respectively.*

Sodium sulphate mixed with alumina is not decomposed even at a white heat, but is decomposed if steam is admitted. In Tilghman's patent of 1847 (see p. 193) this process was also described. Wagner (Jahresb. 1865, p. 328) found that on working in a muffle (that is, excluding the  $\text{CO}_2$ , which acts upon the aluminate), even with three equivalents of  $\text{Al}_2\text{O}_3$  to one of  $\text{Na}_2\text{SO}_4$ , at most only 40 per cent. of the sulphate could be converted into aluminate, the muffle being very strongly corroded. Bauxite behaves similarly; ferric oxide acts better, but only at an extremely high temperature, hardly obtainable in manufacturing-practice. The soda of the sulphate is easily convertible into aluminate if coal is added to the mixture and then heat applied; but bauxite, which always contains iron, cannot be used in this way, because with it the well-known ferro-sodic sulphide is constantly formed. The recommendation of the process by Balard (Hofmann, Report by the Juries, 1863, p. 69) takes no account of this.

Siermann (Engl. pat. No. 356, 1878) heats a mixture of alkaline sulphate with alumina in contact with air.

*Bauxite* is a connecting-link between diasporé (pure aluminium hydrate) and brown hematite; the more the iron predominates in it, the more the white colour passes into brown. It was originally found in France near the village of Les Baux; in the departments of Var and of the Bouches du Rhône, from Tarascon to Antibes,

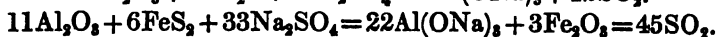
a distance of 100 miles, many deposits are found, some of them several dozens of yards thick. Deposits are also found in the departments of the Hérault and the Ariège. Very good bauxite has been found at Hadamar in Hessa. Very important deposits were found by Flecker in the Austrian province of Krain, on the Sava in Wochein, and on the Feistritz. This mineral, also called wocheinite, is of dense earthy structure, whilst the varieties occurring in France, and also in Ireland (at Irish Hill and Straid, co. Antrim), are oolitic conglomerates. The analyses given below and on p. 213 exemplify the varying proportions of alumina and ferric oxide; besides the constituents mentioned here, the bauxites contain traces of lime, magnesia, sulphuric, phosphoric, titanic, and vanadic acids.

	Irish Hill (Spence).		Glenravel (Hodges).
$\text{Al}_2\text{O}_3$ .....	48.12	43.44	61.89
$\text{Fe}_2\text{O}_3$ .....	2.36	2.11	1.96
$\text{SiO}_2$ .....	7.95	15.05	6.01
$\text{TiO}_2$ .....	...	...	2.32
$\text{H}_2\text{O}$ .....	40.33	35.70	27.82
	<hr/> 98.76	<hr/> 96.30	<hr/> 100.00

*Decomposition of sodium sulphate by alumina with the assistance of reducing gases.*—This is the process of C. R. Claus, Engl. pat. 4311, 1891, already described on p. 195, as it starts from NaCl.

Also Baker's patent (No. 2866, 1870), according to which sodium sulphate is heated with alumina and coal (comp. next chapter), might be entered here.

Peniakoff (Germ. pat. 80063) ignites bauxite, aluminium sulphate or other aluminium compounds with alkaline sulphates in presence of alkaline sulphides or of pyrites; this is to produce sodium aluminate and sulphur dioxide:



The  $\text{SO}_2$  is best used by mixing with air for manufacturing  $\text{Na}_2\text{SO}_4$  and chlorine [by the Hargreaves process?], or is made to act on NaCl in presence of well-known oxygen carriers like  $\text{BaO}_2$  [in what way?].

*Decomposition of sodium sulphate by coal, bauxite, and ferric oxide.*—Behnke (Germ. pat. 7256, 1879) heats all four materials

*Analyses of Bauxite.*

(Partly from Biedermann, in Hofmann's 'Bericht,' i. p. 619.)

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>	<i>f.</i>	<i>g.</i>	<i>h.</i>	<i>i.</i>	<i>k.</i>	<i>l.</i>
Alumina .....	60	75	63.16	72.87	44.4	54.1	64.6	45.77	55.61	56.0	76.3
Ferric oxide .....	25	12	23.55	13.19	30.3	10.4	2.0	18.97	7.17	6.2	8.4
Silica .....	3	1	4.15	4.25	15.0	12.0	7.5	6.41	4.42	11.0	14.9
$\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$ .....	...	...	0.79	0.78	...	...	...	0.38	...	...	...
Water .....	12	12	8.34	8.60	9.7	21.9	24.7	27.61	32.33	26.4	...
Calcium carbonate ...	...	...	...	...	...	...	...	0.65	0.39	...	...

*a* and *b* from Les Baux (Ste.-Claire Deville); *c*, dark wocheinite; *d*, light ditto (Drechsler); *e*, reddish brown, *f*, yellow, *g*, white bauxite from Feistritz (Schnitzer); *h* and *i*, Hadamar bauxite (Dingler's Journ. exptl. p. 273); *k*, bauxite from Klein-Steinheim (Baden), analyzed by Bischof; *l*, the same, calcined.

Further analyses by Mayer and Wagner in Fischer's Jahresb. 1883, p. 430.

together, or first the  $\text{Na}_2\text{SO}_4$  and coal by themselves. The addition of ferric oxide is said to greatly promote the reaction, by forming  $\text{FeS}$ , which is separated from the alkaline aluminate by dissolving this with water, and is roasted; the resulting ferric oxide is used over again.

Fleischer (Germ. pat. 62265) adds to 1 mol.  $\text{Na}_2\text{SO}_4$  1 mol. alumina (in the shape of bauxite), to form  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3$ , and rather more than 1 mol. ferric oxide (including that already contained in bauxite); further at least 3 mols. carbon (as coal), to reduce the ferric acid to  $\text{FeS}$ , and sufficient limestone to provide 2 mol.  $\text{CaO}$  to 3 mol.  $\text{SiO}_2$  (contained in the bauxite), and  $\frac{1}{4}$  mol.  $\text{CaO}$  to 1 mol.  $\text{Al}_2\text{O}_3$ . This mixture is to be heated to a moderate red heat, either in an open furnace, covered with coal, or else in closed vessels; when the proper heat is once attained, half an hour suffices for completing the reaction. The mass is allowed to cool down protected from contact with air, so that the  $\text{FeS}$  is not burned; the alkaline aluminate is then obtained by lixiviation, and is found to contain but little sodium sulphide and traces of lime. The patent describes its purification and the preparation of alumina therefrom.

Instead of decomposing the sodium aluminate by  $\text{CO}_2$ , in which case a modification of alumina not easy soluble in acetic acid is formed, Löwig Brothers (German patent No. 93, 1877) add milk of lime to an aqueous solution of sodium aluminate, whilst heating it, till the liquid has become completely caustic and all the alumina is precipitated; then caustic alkali remains in solution, and a perfectly insoluble compound of  $\text{Al}_2\text{O}_3$  with  $3\text{CaO}$  is precipitated. The latter is separated from the caustic lye, divided into two equal parts, one half is completely dissolved in hydrochloric acid, while the other half, made into a cream with water, is added until a filtered sample shows slight traces of alumina in solution. Calcium chloride passes into solution; and a modification of aluminium hydrate remains behind, which is well adapted for decolorizing, especially sugar-liquors, and is also readily soluble in acetic acid. An additional patent, No. 1650, describes the preparation of sodium aluminate from bauxite or (more correctly) cryolite; but as it starts from fusion with sodium carbonate, and its proper object is the preparation of pure alumina along with caustic soda, we must refer to the patent itself. The reactions employed in Löwig's process are:—



- I.  $\text{Na}_2\text{Al}_2\text{O}_6 + 3\text{Ca}(\text{OH})_2 = 6\text{NaOH} + \text{Ca}_3\text{Al}_2\text{O}_6$ .  
 II.  $\text{Ca}_3\text{Al}_2\text{O}_6 + 12\text{HCl} = 3\text{CaCl}_2 + 2\text{Al}_2\text{Cl}_6 + 6\text{H}_2\text{O}$ .  
 III.  $\text{Ca}_3\text{Al}_2\text{O}_6 + \text{Al}_2\text{Cl}_6 + 6\text{H}_2\text{O} = 3\text{CaCl}_2 + 2\text{Al}_2(\text{OH})_6$ .

*By Silica.*

Water-glass (sodium silicate) was long since made by melting together sand, sodium sulphate, and coal,  $\text{SO}_2$  escaping; but as the material of the furnaces was quickly destroyed, most manufacturers prefer making water-glass by fluxing sand with sodium carbonate. From the water-glass, by introducing  $\text{CO}_2$ , an aqueous solution of sodium carbonate can be obtained, but much more expensively than by Leblanc's process; for the furnace-process is not done away with, and carbonic acid is not to be had for nothing. The proposal to employ the separated silica over again for decomposing sulphate does not mend matters, since ordinary sand will do as well. From the solution of water-glass also caustic soda, along with calcium silicate, can be obtained by boiling with lime. One of the greatest difficulties in this process is the washing of the gelatinous hydrate of silica. The separation of the calcium silicate from the caustic lye is said to be less difficult: but here also great difficulties must exist; for this seemingly advantageous plan for making caustic soda is not employed, although it has been known for generations. In February 1874 the St.-Gobain Company took out a French patent for this old process. It prescribes melting 71 parts of sodium sulphate, 80 parts of Fontainebleau sand, and 8 or 9 parts of small coal in a closed crucible, dissolving, and making from the solution either sodium carbonate by means of  $\text{CO}_2$ , or caustic soda by means of lime. The  $\text{SO}_2$  escaping during the melting is to be used in sulphuric-acid making (but *how*, in the presence of carbonic acid?). It is almost needless to say that this process has not been carried out to any great extent.

*By Lead or Zinc Compounds.*

Baudrimont and Pelouze noticed 1833 (Wagner's 'Regesten,' p. 53) that, on heating sodium sulphate with galena in the presence of silica, sodium plumbate ( $\text{Na}_2\text{PbO}_2$ ) was formed. How this reaction is to be practically carried out is not stated in our authority; but the addition is made that blende may be substituted for galena.

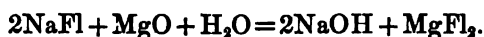
Closson (Engl. pat. 5481, 1882) treats a hot solution of sodium sulphate with milk of lime and plumbic oxide, precipitates the dissolved lead by sodium carbonate or sulphide, or by electrolysis, and separates the undecomposed sulphate during the evaporation of the liquor.

*By Hydrogen Fluoride.*

Among the three new alkali-making processes which Weldon patented as No. 628, 1866, there is one employing hydrofluoric acid, which comprises the following stages :— 1st. Sodium chloride and magnesium sulphate are mutually decomposed, either in the dry way or, better, by mixing their solutions and cooling down to  $-4^{\circ}\text{C}$ . ; sodium sulphate crystallizes out ; and the mother liquor, by boiling down the  $\text{MgCl}_2$  and heating, is decomposed into  $\text{MgO}$  and  $\text{HCl}$  [incompletely !] 2nd. The  $\text{Na}_2\text{SO}_4$  is treated with aqueous solution of  $\text{HFl}$ , which causes the formation of hydrosodic sulphate and sodium fluoride :



The treatment takes place in the cold in a suitable vessel lined with lead or gutta-percha &c., and is finished by stirring for a few minutes ;  $\text{NaFl}$  settles down as a dense precipitate ;  $\text{NaHSO}_4$  remains in solution. 3rd. This  $\text{NaFl}$  is decomposed by the magnesia obtained in 1, by boiling in an aqueous solution, caustic soda and magnesium fluoride being thus formed :



4th. The  $\text{MgFl}_2$  from the 3rd operation is decomposed by the  $\text{NaHSO}_4$  from the 2nd into magnesium sulphate, hydrofluoric acid, and sodium fluoride :

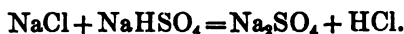


This also is said to take place at a slightly elevated temperature ; and “ thus all the materials, except salt and coal, are recovered ” [in theory].

The following is mentioned as a still shorter method :— 1st. Sodium fluoride is decomposed by superheated steam into caustic soda and hydrofluoric acid,

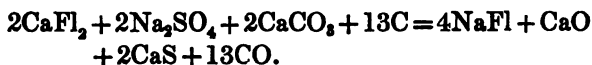


2nd. As in the 2nd stage of the preceding, sodium sulphate is decomposed with the HFl from No. 1 into hydrosodic sulphate and sodium fluoride, the latter serving again for the 1st operation. 3rd. The hydrosodic sulphate is by common salt decomposed into sodium sulphate and hydrochloric acid, and the former employed for the 2nd operation :

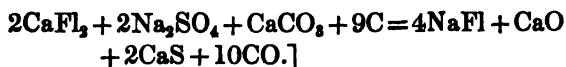


Neither of these plans has found, or is likely to find, any practical application.

According to Jean (Compt. Rend. lxvi. p. 801), by melting 100 parts of fluorspar with 140 of calcium carbonate, 200 sodium sulphate, and coal in excess, a mass can be obtained which on lixiviation yields a clear solution of NaFl, free from  $\text{Na}_2\text{S}$ , according to the equation :



[This equation is wrong ; but we might put it



The sodium fluoride is easily obtained in the pure state by evaporation and crystallization. Experiments made in my laboratory showed that but little sodium fluoride is formed, and that it can be obtained in a pure state only in the first lixiviation ; the next washing always contains more sodium sulphide, generated by the reaction of the sodium carbonate, formed at the same time, upon calcium sulphide in the presence of air.

#### *By Calcium Phosphate.*

Simpson (Engl. pat. 18835, 1890) dissolves tricalcium phosphate in hydrochloric acid of spec. grav. 1.05 and decomposes the solution with sodium sulphate (or bisulphate). The solution is separated from the calcium sulphate and is boiled down to the consistency of a paste, whereby weak hydrochloric acid escapes ; the remainder of the HCl is removed on heating in a muffle-furnace and is condensed. The mass formed in the furnace is a fused mixture of sodium phosphate and chloride, which is run

into water: thus a solution of spec. grav. 1.3 or 1.35 is obtained, which is allowed to cool, when the sodium phosphate crystallizes out. It is re-dissolved to spec. grav. 1.18 and is causticized by lime: thus caustic soda is formed, together with insoluble tricalcium phosphate, which returns into the process. It is also possible to obtain dicalcium phosphate, by dividing the process into two stages. The calcium sulphate contains a little phosphate, and is either employed as manure, or is transformed, by heating with coal, into sulphide, which is converted into soluble sulphhydrate in the usual way, and is then separated from the insoluble calcium phosphate.

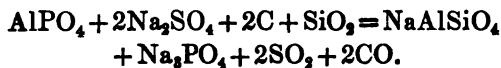
Ody (Engl. pat. 5425, 1892) describes nothing but the well-known precipitation of  $\text{CaSO}_4$  from  $\text{Na}_2\text{SO}_4$  with monocalcium phosphate; the sodium phosphate formed is to be treated with lime, in order to form  $\text{NaOH}$  and recovered tricalcium phosphate.

Basset and Baranoff (Engl. pat. 21447, 1894) also decompose monocalcium phosphate by sodium sulphate into sodium phosphate and calcium sulphate, and again the sodium phosphate by caustic lime into caustic soda and tricalcium phosphate.

The novelty of their process consists in the preparation of the initial substances. They heat calcium sulphate and sulphite with carbon in a retort, collecting the  $\text{CO}_2$ . The residual  $\text{CaS}$  is decomposed by this  $\text{CO}_2$  in the moist state, and the  $\text{H}_2\text{S}$  evolved thereby is burned, collecting the  $\text{SO}_2$  in a gas-holder. This  $\text{SO}_2$  is partly utilized for converting common salt mixed with porous substances into  $\text{Na}_2\text{SO}_4$  by a process similar to Hargreaves', and partly for decomposing tricalcium phosphate into soluble monocalcium phosphate and calcium sulphate. The latter, together with the calcium sulphate previously obtained, is again converted into calcium sulphide as first described.

#### *By Aluminium Phosphate.*

G. E. Davis (Journ. Soc. Arts, 1877, p. 633) ignites commercial aluminium phosphate (Redondo phosphate) with sand, saltcake, and small coal, utilizing the escaping  $\text{SO}_2$  [which will prove practically impossible]. Thus sodium aluminium silicate and sodium phosphate are formed:



By lixiviation trisodium phosphate is obtained, coloured green by ferro-sodium sulphide; it is converted into ordinary disodium phosphate by phosphoric acid, or by lime into caustic soda, or by calcium carbonate into sodium carbonate. The calcium phosphate was to be sold as manure. [The soda contained in the insoluble sodium aluminium silicate would have been entirely lost.]

*By Calcium Bisulphite.*

Gutzkow (Engl. pat. 4122, 1879) precipitates calcium sulphate by sodium sulphate from a solution of calcium bisulphite. By distilling the solution of sodium bisulphite half of the  $\text{SO}_2$  is liberated; the residual sodium sulphite, treated with caustic lime, yields caustic soda and again calcium sulphite.

Gutzkow has made some communications on his process in Dingl. Journ. ccxxxvi. p. 148. The distillation of the solution of sodium sulphite had to be abandoned, owing to troublesome incrustations of calcium sulphite and the slowness of the operation. Instead of this, milk of lime was added to the solution, thus forming a solution of caustic soda, still containing sodium sulphite and sulphate, together with a precipitate of  $\text{CaSO}_3$ , which is returned into the process by mixing it with  $\text{Na}_2\text{SO}_4$  and passing  $\text{SO}_2$  into the mixture. [This process may have been successful under very special conditions, where the removal of  $\text{SO}_2$  is the principal object; but it is obviously not fit for general use.]

*By Calcium Oxalate.*

J. J. Alsberge (private communication, July 1893) decomposes sodium bisulphate with calcium oxalate, separates the  $\text{CaSO}_4$  from the acid sodium oxalate, and decomposes this by lime into caustic soda and calcium oxalate, which is used over again.

*By Phenol.*

Staveley (Engl. pat. 17657, 1887) produces from the crude phenols, obtained in the distillation of coal-tar or from blast-furnace gases, a solution of calcium carbolate and cresylate, which with sodium sulphate yields a precipitate of  $\text{CaSO}_4$ ; the phenols remain in solution as sodium salts, and these are decomposed by carbonic acid. After settling, two layers are found to be

formed—at the bottom a solution of sodium carbonate containing 1 or 2 per cent. phenols, and above it a layer of liquid phenols, which is used as before. The inventor has described his process in detail in Journ. Soc. Chem. Ind. 1888, p. 807, and there states that the decomposition of  $\text{Na}_2\text{SO}_4$  by calcium phenolates can be carried to 96 per cent. He also states means for reducing the loss of phenols to the smallest possible amount, but he admits that such a loss cannot be entirely prevented, and that consequently his process is more expensive than the Leblanc process, except for utilizing otherwise worthless solutions of sodium sulphate.

The Chemische Fabrik Grünau (Germ. pat. 48270) describes a very similar process for converting alkaline sulphites and sulphates into carbonates by means of phenol, cresol,  $\alpha$ - and  $\beta$ -naphthols.

*By Calcium Saccharate.*

Closson (Engl. pat. 1721, 1881) decomposes alkaline sulphates by calcium saccharate into calcium sulphate and alkaline saccharate; the latter is decomposed by  $\text{CO}_2$  into alkaline bicarbonates and sugar, which is to be used over again [!].

*By Calcium Acetate, &c.*

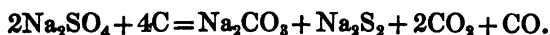
Frerichs (Engl. pat. 9793, 1890) adds calcium acetate to  $\text{Na}_2\text{SO}_4$ , filters from the  $\text{CaSO}_4$ , and submits the sodium acetate to destructive distillation, in which acetone is given off and sodium carbonate remains behind. The decomposition by calcium acetate was proposed as early as 1778 by Crell, in 1822 by Millet, afterwards by Mollerat and Payen and by Lampadius. Kirwan in 1789 proposed *lead acetate*, Anthon in 1842 *barium acetate* (Wagner's 'Regesten,' p. 45).

## CHAPTER XIII.

MANUFACTURE OF SODA FROM SODIUM SULPHATE  
AFTER REDUCING IT TO SULPHIDE.

## I. WITHOUT SEPARATING SULPHIDE AS SUCH.

By merely *heating sodium sulphate with coal* it was formerly believed that soda could be manufactured. At a very early period a sulphide containing carbonate was thus obtained, which by lixiviating, boiling down, fishing out, and again calcining was made richer in carbonate. This process is described in a notebook of Tennant's works, dating from 1800 (Mactear, Report, p. 18). According to a paper of Mactear's in the 'Journal of the Chemical Society,' 1878, vol. ii. p. 476, Liebig proposed to the same firm, by a letter dated July 11, 1839, heating of sulphide with coal to 300° C. as the best of all soda-making processes; he stated that first oxalate and acetate were formed, and these on heating passed over into carbonate. Berzelius, Graham, and Gay-Lussac approved the process: the latter made experiments on a large scale at Chauny; others were made at St. Rollox; but in neither case was success obtained. Liebig is said to have ascribed this to the fact that the decomposition takes place in another way than that which he had imagined at first, viz. :



Gossage (Engl. pat. 3295, 1869) tried to obtain caustic soda by running melted sodium sulphate through red-hot coke; the sulphur was to escape in the free state, and to be condensed as such.

*By Calcium Carbonate and Coal.*

This is Leblanc's process.

*By Barium Carbonate and Coal.*

G. Reinard (Wagner's Jahresb. 1858, p. 118, 1864, p. 167) proposed employing this instead of calcium carbonate for Leblanc's process in countries where native barium carbonate "occurs in very large quantities," in the proportion of 100 sulphate, 200  $\text{BaCO}_3$ , and 75 bituminous coal. The residue from lixiviation, consisting of (hypothetical!) barium oxysulphide, thiosulphate, and carbonate, was to be worked for baryta salts. From the outset, as Hofmann ('Report by the Juries,' p. 32) justly says, it is not apparent what is to be gained by replacing calcium carbonate by a compound having more than thrice its atomic weight, entailing the heating and manipulation of a much greater weight and bulk of material, merely to obtain compounds less adapted than native barium carbonate for the preparation of other barium salts. [The ratio of the atomic weights, however, is strongly exaggerated here; the atomic weight of  $\text{BaCO}_3$  is not "more than thrice" as much as that of  $\text{CaCO}_3$ , but as 197 to 100; and only this proportion, not that between the elements Ba and Ca, can be taken into account here.] Reinard's proposal is further vitiated by the same error which has rendered many other proposals in the "baryta industry" abortive, viz. the assumption that native barium carbonate occurs anywhere in "very large quantities," approaching those of limestone. The only known larger deposits near Hexham in Northumberland are already exhausted to a great extent; the price of anything like a good quality, delivered at Newcastle, is at least ten times as much as that of limestone even in less favourably situated places. Moreover, in this special case Wagner (his Jahresb. 1858, p. 168), even when employing twice the quantity of barium carbonate, in experiments on a small scale, obtained very unsatisfactory results, especially very much sulphide in the liquors.

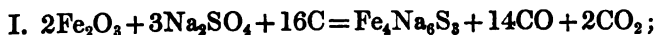
*By Iron or Ferric Oxide with Heat.*

We have already seen (Vol. II. p. 446) that Malherbe's soda-making process of 1778 is founded upon this principle. This process is also known as Alban's, because Alban carried it out as a manufacture. He fluxed sodium sulphate with coal to form sulphide, and added scrap iron; the mass of iron sulphide and caustic soda, formed with the assistance of the oxygen in the fire-

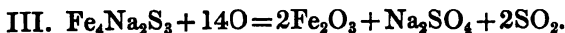


gas, was exposed to the air till it fell to powder, and then lixiviated. In 1828 F. E. Siemens, at Pyrmont, made soda on the large scale by a similar process; but he decomposed the  $\text{Na}_2\text{S}$  by a mixture of manganese peroxide and iron (Wagner's 'Regesten,' p. 36). This process forms the natural transition to that of E. Kopp, who changed the original process of Malherbe only so far as to add ferric oxide instead of metallic iron, which had first to be oxidized by the fire-gases. He certainly also aimed at utilizing the sulphur of the sulphate, of which Malherbe says nothing. Patents were taken out by Blythe and Kopp, No. 2119, 1854, and No. 340, 1855; and the process was actually employed for some time at the works of Messrs. Blythe and Benson at Church near Manchester. It was soon, however, given up again as useless. Kopp himself has described it at length (Ann. Chim. Phys., Sept. 1856, p. 21):—  
"125 kilog. dry sodium sulphate are mixed with 80 kilog. ferric oxide (for the first operations in the shape of native iron-ores, or smiths' scales, or even metallic iron, afterwards as recovered ferric oxide) and with 55 kilog. of small coal. In no case ought less than 5 parts  $\text{Fe}_2\text{O}_3$  to be present to 9 parts of dry  $\text{Na}_2\text{SO}_4$ . The mixture is worked in an ordinary black-ash furnace; it exhibits about the same appearances as a batch of Leblanc black ash, and, in a fiery molten state, is drawn into an iron bogie, where it is covered and cooled, yielding a very dense evenly crystalline mass, of a coppery lustre on the surface. It cannot be lixiviated directly, because it swells up very much and yields green badly settling liquors containing much caustic and sulphide. But lixiviation is easy if the balls are first allowed to fall to pieces in the air under the influence of its oxygen and carbonic acid—still more so if cold moist carbonic acid (from a coke-oven) is admitted into a brick chamber, in which the balls rest on an iron grating, the powder falling through the same. A ball of 250 kilog. requires one cubic metre of space, 8 to 10 days' time, and about 10 kilog. coke for falling. Now, on lixiviating with water at  $30^\circ$  to  $40^\circ$  C., a perfectly clear solution of carbonate is obtained, along with a heavy precipitate consisting mostly of iron sulphide [and soda]. The liquor, without any boiling down, yields very good soda crystals, or by evaporating to dryness and calcining can be converted into ash containing from 80 to 95 per cent.  $\text{Na}_2\text{CO}_3$ . The  $\text{FeS}$  is drained and pressed into bricks; if at all dry, it takes fire even below  $100^\circ$  C., and burns like tinder. It is roasted on cast-iron plates,

but better in a muffle; the  $\text{SO}_2$  is conveyed into a vitriol-chamber, and the sulphuric acid made from it used for preparing sulphate; the residue of ferric oxide is employed over again in the first process. It contains still one-third of all the soda employed; but this is not lost, as it is recovered on re-employing the ferric oxide. Only the mixing proportions must be altered in that case—say, to 125 kilog. sulphate, 140 kilog. recovered ferric oxide, 70 to 75 kilog. coal. The oxides of manganese or zinc may also be used, but less advantageously." Kopp represents the reaction thus:—



On oxidizing  $\text{Fe}_4\text{Na}_2\text{S}_3$  in the damp air and calcining, there are formed (leaving out intermediate products):—



Kopp's process was soon after thoroughly investigated by Stromeyer in his laboratory (*Ann. Chem. Pharm.* cvii. p. 333), and, on the whole, received a favourable judgment. He, however, entirely disagrees with Kopp's theoretical explanations, especially touching the part played by oxygen, the action of which is even injurious, especially by the formation of thiosulphate, overlooked by Kopp. The liquor obtained from the melted mass contains, beside sodium sulphide, hydrate and carbonate. Stromeyer states that the formula of the double sulphide arising in the process is  $\text{Fe}_2\text{Na}_2\text{S}_3$  [Kopp, in Wurtz's 'Dictionnaire,' ii. p. 1578, adopts the same formula, and thus gives up his own]; with water it forms a black jelly possessing extremely emulsive properties. It is decomposed by moisture and carbonic acid; and then with water a non-emulsive clear solution of almost pure sodium carbonate is obtained; the precipitate, however, always retains  $\text{Na}_2\text{S}$  in variable quantity. On treatment with  $\text{CO}_2$  much  $\text{H}_2\text{S}$  is always given off; Kopp's second equation, therefore, cannot be right, and much sulphur must be lost. As the result of his many experiments, Stromeyer proposes only employing 1 molecule of  $\text{Fe}_2\text{O}_3$  (80) to 3 of sodium sulphate (213); further, to work in furnaces with cast-iron bottoms, because the fluxing mass strongly acts upon fireclay, and to employ  $\text{CO}_2$  as free as possible from oxygen.

Perhaps in consequence of Stromeyer's paper, and of the exact description given by Kopp himself, this process excited much

attention and raised far greater expectations of success than most other processes hitherto known. It was expected that in this way the sulphur, which in Leblanc's process is lost, could be continually reintroduced into the process. But already in 1863 (Report by the Juries, p. 31) Hofmann points out that Kopp's process, "although irreproachable so far as regards the conversion of sodium sulphate into carbonate [this is certainly not the case!], yet is very defective with respect to the re-utilization of the sulphur; his sulphide of iron contains too much sodium sulphide to yield, when burnt, any considerable quantity of  $\text{SO}_2$ , which, moreover, is accompanied by an enormous bulk of nitrogen, corresponding to the oxygen combining with the iron and the sodium sulphide. Its utilization in vitriol-chambers would be out of the question." Kopp (*apud* Wurtz), in referring to his own process, reproduces Hofmann's opinion without any remark, and thus makes it his own, adding that since the discovery of processes for recovering sulphur from tank-waste the motive for his process had ceased to exist.

According to experiments made by Waldeck (Dingl. Journ. cxcii. p. 417), not only fireclay, but also cast-iron, which Stromeyer had recommended for the furnaces, is acted upon "in a truly frightful way"; nor could lining the crucibles with a mixture of powdered coke and tar protect them. The original percentage of iron in the mixture is increased fourfold by that action. Even this would make Kopp's process practically impossible; but another point must be regarded, which is only incidentally touched upon by Waldeck when stating that the yield of soda from the fluxed mass was only 9.4 per cent. instead of 36 per cent. The author of this work, who in 1865 made a long series of experiments with Kopp's process in a furnace specially built for the purpose, came to the conclusion that the process was impracticable, because not merely does one-third of the soda always remain in the insoluble residue, as admitted by Kopp himself, but, under the ordinary conditions of a reverberatory furnace, the re-formation of sulphate in the batch cannot be avoided; owing to this, the conversion of the sulphate into carbonate is so incomplete. Experiments in closed crucibles succeeded better. In this case soda-ash testing 95 per cent. carbonate could be obtained; but the yield was always bad. The treatment with  $\text{CO}_2$  had always to take place as much as possible in the absence of air; otherwise very much thiosulphate was formed. In spite of its notorious failure, Kopp's process was

for a long time (and in some treatises published only quite recently it is still) stated to be a most hopeful one, which might possibly drive Leblanc's out of the field—and this, although the only important advantage claimed for it over that of Leblanc, viz. the recovery of the sulphur, was already denied by Hofmann and given up by Kopp himself. Looking at the extremely bad yield and the destructive corrosion both of fireclay and iron by the fluxing mixture, no future can be predicted for Kopp's process.

A modification of the ferric-oxide process, returning to some extent in the direction of Malherbe's, was patented by Bowron and Robinson as No. 3044, 1863. "First sodium sulphide is to be made, and then ferric oxide introduced." The principal intention was that of making the more valuable caustic soda. The author, who had to conduct the trials for carrying out this process on a manufacturing scale, convinced himself of its uselessness. Whatever conditions of work might be observed, there always remained a large quantity of sodium sulphide undecomposed. This could be removed by boiling with  $\text{MnO}_2$ ; but it only changed into thiosulphate, which cannot be separated from caustic soda by crystallization. The removal of the thiosulphate by barium chloride (Robinson's patent, 2801, 1865) proved quite impracticable. Besides, a great deal of sodium sulphate and carbonate, and in the residue much undecomposed sulphide, were present; the latter, as in Kopp's process, was to be turned to use by burning and employing the residue again; but this failed, from the same causes.

Macfarlane (Engl. pat. 126, 1863) ignites dried copperas with salt in a current of air; chlorine escapes, and a mixture of sodium sulphate and ferric oxide remains, which is mixed with coal and worked up as in Kopp's process; the hearth employed is of quick-lime mixed with slightly basic slags and impregnated with sodium sulphide by melting a mixture of sulphide and coal upon it. The batch is treated as in Kopp's process; the remaining sulphide of iron is oxidized to copperas in moist air [which, it is well known, only takes place very incompletely]; and this is employed again for calcining with salt. Hargreaves and Robinson (patents 2982 and 3032, 1872, and 764, 1873) add to Leblanc's mixture ferric oxide, flux it in crucibles with holes in the bottom, lixiviate the mass, oxidize by exposure to the air the iron sulphide formed, and extract the product by hydrochloric acid. Afterwards they patented mixing saltcake and coal with a salt of iron, manganese,

or zinc, heating up to the formation of a coherent, porous, not fluxed lump, dissolving out the soda, burning the sulphides into oxides, and using them as above.

Letelié (French pat. 211058) describes a very complicated process, combining the processes of Macfarlane, Harran, Kopp, and Longmaid. From sodium sulphate, ferric oxide, and coal, the well-known double sulphide is to be prepared; this is to be carbonated, lixiviated, the residue is to be roasted, furnaced with common salt to produce chlorine, and so forth.

Don (Engl. pat. 2111, 1870) once more patents the heating of saltcake with coal and manganese or ferric oxide, and treatment of the product with  $\text{CO}_2$ .

Haydn Mozart Baker (Engl. pat. 2866, 1870) heats saltcake with coal and clay or alumina, extracts the sodium aluminate and decomposes it with  $\text{CO}_2$ .

## II. AFTER PREVIOUS PREPARATION OF SODIUM SULPHIDE.

### *Preparation of Sodium Sulphide.*

We here mention only such processes which are intended to furnish a comparatively pure sodium sulphide for the purpose of alkali manufacture, but not those by which commercial sodium sulphide is made from Leblanc waste (comp. Vol. II. p. 827). The properties and preparation of the various hydrates of sodium sulphide, crystallized from alcohol, have been explicitly described by Göttig, in Journ. f. prakt. Chem. [2] xxxiv. p. 229.

Arrott (Engl. pat. No. 1370, 1859) proposes melting 4 parts of sodium sulphate with 1 part of coal in a cupola, which of course is heated by special fuel. Laming (like many others) ignites 2 parts of saltcake with 1 part of coal or coke in a closed vessel. Gossage (patent No. 2612, 1859) employs the same proportions, but in a close roaster, in order to exclude re-oxidation. Fifty parts by weight of slack per cent. of saltcake, or 33 per cent. of powdered coke, is to be taken, the mass to be constantly stirred, but the heat not increased up to the fluxing of the mass; the  $\text{CO}_2$  arising in the process is to be drawn away by a fan-blast or similar apparatus, and employed for decomposing the sodium sulphide. The batch must be drawn as quickly as possible, and protected from the air. Wilson (patent No. 1361, 1859) fluxes a mixture of 4 cwt. saltcake,  $\frac{1}{4}$  cwt. of barium sulphate, and  $2\frac{1}{2}$  cwt. small coal

or 2 cwt. coke powder in an ordinary reverberatory furnace, or, still better, in a revolving cylinder furnace, in which less heavy spar need be used, as the air has less access, than in a furnace worked by hand. Also Jean, *Monit. Scient.* 1869, p. 1007, proposes making  $N_2S$  by the help of heavy spar, but employs a very great deal of it, viz. 25 kilog. sodium sulphate, 75 kilog. barium sulphate, 10 kilog. charcoal-dust, and 15 kilog. coal-dust; the operation takes place in an ordinary black-ash furnace which is said not to be corroded by this mixture. Wilson (*loc. cit.*) further describes an apparatus for running melted saltcake through a column of coals or coke at a cherry-red heat, in order to convert it into sulphide. A laterally attached deep furnace supplies the necessary heat as a gas-generator; the saltcake is charged onto the top of the coke-column, on a perforated arch, and there fuses of its own accord; the gases afterwards travel through a tower filled with continually moistened pebbles in order to cool the  $CO_2$  and return any sodium salts carried away; at the end of the apparatus a fan-blast causes the movement of the gases and the air throughout the whole apparatus. The CO formed at the same time is burnt in the upper portion of the tower by air admitted for this purpose. The  $CO_2$  is then employed for making carbonate from the sulphide, or else for turning carbonate into bicarbonate, which is itself employed for converting sulphide into carbonate.

It is very probable that such an apparatus would be destroyed after a short lapse of time. A similar process was patented by Claus (No. 819, 1869), who attempted to preserve the cupola in which the reduction of the fused saltcake takes place by means of a water-jacket. The sulphide is partly tapped off at the bottom in a fluid state; but a great part is volatilized and is passed along with the products of combustion into a scrubber, through which a solution of sodium sulphide is run down; in this the volatilized portion is condensed and at the same time converted into carbonate by the carbonic acid formed in the reducing process. Another proposal by Claus (No. 2616, 1869) refers to the manufacture of sodium or potassium sulphide by means of gaseous fuel, carefully kept free from uncombined oxygen, so that but very little thiosulphate can be formed. A third proposal is this—to make barium sulphide from barium sulphate, dissolve it in water, and decompose a solution of sodium sulphate by the same, when sodium sulphide will be formed and barium sulphate be recovered. This

process (which is far too expensive to be of practical importance) was once more proposed, as new, by Vincent (*Compt. Rend.* 1877, lxxiv. p. 701). Barrow's patent (No. 10491, 1886) contains nothing new whatever. The *Chemische Fabrik Buckau* (Germ. pat. 57707) decomposes a mixture of potassium and sodium sulphate, made from Stassfurt salts, by BaS, converts the mixed alkaline sulphides in aqueous solution by  $\text{CO}_2$  into bicarbonates, and separates the potassium bicarbonate in the shape of crystals from the more soluble sodium bicarbonate.

Maistre (Fr. pat. 208471) patents as "new" the reduction of BaS from native barium sulphate by coal, and application of this to convert  $\text{Na}_2\text{SO}_4$  into  $\text{Na}_2\text{S}$ .

Willans (Engl. pat. 293, 1860) prepares  $\text{Na}_2\text{S}$  from saltcake without coal, simply by CO and steam in a red-hot furnace. We shall see that several other inventors produce  $\text{Na}_2\text{S}$  by gaseous CO from  $\text{Na}_2\text{SO}_4$ .

The process with sodium sulphide and carbonic acid has been most thoroughly worked out by the celebrated inventor of the manganese-recovery process, Walter Weldon, who spent years upon it and believed he had attained his object, when, on Aug. 28th, 1876, and Feb. 2nd, 1877, he took out a series of patents in reference to it (Nos. 3370 to 3390, 1876, and 444 and 445, 1877). His process commences with a very original way of making the sodium sulphide. Saltcake, made in any suitable way, is fused in a Siemens' regenerative furnace; and the combustion-gases of this furnace are at the same time employed in a second furnace, in which the sulphide is made. The first furnace is placed at such a height that the fused saltcake can run into the manhole of the second furnace. This second furnace, in which the saltcake is reduced to sulphide, is the principal thing. It is a revolving cylinder furnace such as are now generally used for the ordinary black-ash process. [When trying the process on the large scale no revolving furnace was employed, owing to the great cost, but a hand-furnace; in case of success revolvers would have been used. In his last patent Weldon reverts to the use of a hand-furnace exclusively.] As all brick-work and iron is very strongly corroded by melting sodium sulphide, the furnace had to be lined with a more refractory material. As such, bricks made of powdered coke with a little tar, moulded with a very strong pressure and heated to a red heat in a close furnace, are used; they are set in a

mixture of the same materials. This lining has turned out entirely successful in practice, so long as the fire-gases were free from oxygen. That end of the furnace through which the fire-gases enter can be closed air-tight. For this purpose the "eye," always hung in cylinder furnaces between the fireplace and the cylinder, is so arranged that it can be promptly moved aside and a solid disk of the coke mixture can be put in its place; the latter is surrounded by an iron ring carrying a broad flange, which is firmly connected by bolts with the central opening of the cylinder; thus the disk revolves with the cylinder and forms an air-tight closing. The outlet-hole at the other end of the cylinder is continued into a fire-flue, which is divided into two parts, so that by suitable dampers the gases can either be taken to the chimney or the carbonic-acid gas can be kept for special use in suitable apparatus or employed directly. Also the furnace from which the cylinder furnace is supplied with fire-gases, be it the saltcake-melting furnace or a special gas-producer, is so arranged that the products of combustion can either be conveyed into the cylinder furnace or elsewhere. Now, in the converter, small coke or charcoal [according to the patent of Feb. 2nd, 1877, exactly as much as suffices for forming carbonic acid with the oxygen of the saltcake, viz. 16.9 per cent. of the weight of the saltcake, of course adding the impurities; it is then best to work in a blind roaster and to aspirate the carbonic-acid gas by means of a fan-blast] is brought to a red heat, by admitting fire-gases at one end and allowing them to escape at the other; then the fire-gas is cut off, the entrance-opening closed in the above-described manner, and the exit-opening connected with the apparatus for keeping or employing the carbonic acid; from the furnace, placed higher up, fused saltcake is run onto the red-hot coke or charcoal, and the two are mixed by quick revolutions of the cylinder. The reaction between saltcake and coal thus goes on in a vessel which during this period has only one opening, that for removing the carbonic acid. Weldon has also constructed another, simpler, not revolving furnace for the same object. If the saltcake and the coke have each been sufficiently heated, the reaction between them will be finished without applying any ulterior source of heat; otherwise fire-gas must be again admitted, and in the meantime the other end must be connected with the chimney. Of course, if the carbonic acid is not to be utilized, the exit-gases may always be



allowed to go into the chimney. (The treatment of the sodium sulphide thus prepared by carbonic acid as described by Weldon will be described later on.)

According to information which I subsequently received from Mr. Weldon himself, the above process suffered under the drawback that the pure sulphide, free from polysulphides, thiosulphate, and caustic soda, as it was obtained in his furnace, turned out to be infusible, and could not be removed from the furnaces. This could be remedied by allowing a little air to get into the furnace, but then the carbon-lining burned out very rapidly. [Elsewhere, as we shall see, no such trouble has been experienced.]

Wallace and Claus (Engl. pat. 2842, 1877) provide the furnace intended for making sodium sulphide with a lining of bauxite.

Cl. Winkler (Chem. Ind. 1880, p. 129) gives the following description of the way in which sodium sulphide was manufactured on an extensive scale for a number of years :—Calcined saltcake was mixed with 25 or 30 per cent. coal, and reduced in a small reverberatory furnace at a moderate red heat. The working-door was arranged opposite the fire-bridge, so that the air entering here was drawn away directly into the exit-flue, without acting on the charge. In order to make the furnace resist the action of the fusing mass, the furnace-walls were made of large, smoothly-dressed blocks of marble, the joint being firmly "grouted" with lime. The bottom consisted of a single, dished block of marble, with a laterally drilled-in tap-hole; on this rested the blocks forming the side-walls, which had to be repaired from time to time. By careful heating up a cracking of the stone blocks could be avoided. The fusion took place quickly and smoothly; as soon as superficial fusion had set it, the mass was thoroughly stirred with an iron rake, to prevent, by an excess of coal, the sulphide from burning. As soon as the reduction was complete, the contents of the furnace, which were formerly pasty, turned quite liquid (comp. Weldon's contrary observation, *suprà*). Now a peculiar phosphorescence was noticed, and a shower of sparks indicated a commencing combustion of the sulphide, which, however, could be instantly checked by throwing in a handful of coal-dust. When these phenomena set in, the liquid sodium sulphide was tapped into iron dishes, where it was at once covered with a little coal-dust and a sheet of iron; while still warm, it was broken up into lumps about the size of a man's fist and put into

casks, where it retained its condition for some time. It was at first found difficult to dissolve it, as it could not be crushed on account of its pyrophoric properties, and when the lumps were put in the dissolver as such, the impurities settled upon them as a thick slime. This was avoided by placing the lumps in drums, with sides made of thin staves, half dipping into the water intended to dissolve the stuff, and turned from time to time by means of a hand-crank; thus the slime-covering was always rubbed off.

Esop (*Zsch. f. angew. Chem.* 1889, p. 284) describes the manufacture of sodium sulphide as follows:—150 kil. ground saltcake is mixed with 100 kil. coal-dust. The furnace is 20 feet long, 6 feet 6 inches wide, and 6 feet high, with a fire-brick lining, divided longitudinally into three parts. The fireplace has a grate-surface 2 ft. 9 in. square; it is divided from the working-bed by a fire-bridge, and a back bed follows upon the former without any outward division. The charge is put upon the back bed, where it remains  $1\frac{3}{4}$  hours, during which time the last charge is finished on the front bed. Each charge requires about  $1\frac{1}{2}$  cwt. good firing-coal. At the end the front working-door is opened, and the liquid mass is drawn by means of rakes into iron boxes, which are at once covered up. It weighs 100 to 115 kil., and contains 60 per cent.  $\text{Na}_2\text{S}$ . It should be red and porous, not dense, glassy, or grey; in the fresh state its solution ought to give only a slight opacity with barium chloride. In order to lixiviate it, it is broken up as quickly as possible into pieces of about 4 inches, with caution on account of its caustic property, which are at once thrown into the lixiviating tank and covered with liquor. The apparatus used is a Buff-Dunlop set of five tanks (*Vol. II. p. 585*); the work lasts 24 hours. The strong liquor from tank No. 5 shows spec. gr. 1.285; from No. 4, 1.19; from No. 3, 1.13; from No. 2, 1.05 to 1.075; and from No. 1, 1.007 to 1.03. The mass is washed down to 1 to 3 per cent.  $\text{Na}_2\text{S}$  before being cast out. Every other day a tank can be emptied and re-charged; this produces about 210 cub. ft. of liquor of spec. gr. 1.30, which, after an hour's settling, is sufficiently clear to be run into the crystallizing vessels. Strong liquor is yellow, liquor below spec. grav. 1.075 is greenish. The crystallization in shallow iron coolers takes four or five days, and yields fine yellow or brown crystals of  $\text{Na}_2\text{S}$ ,  $9\text{H}_2\text{O}$ , which are easily detached from the sides of the coolers, and are separated by centrifugal machines from the

mother liquor. This is mixed with fresh liquor of spec. grav. 1.22 to 1.24, and is concentrated to spec. grav. 1.275 by the waste heat of the furnace; it is then again brought to crystallization. The salts formed by oxidation during the evaporation sink to the bottom, and are mixed with fresh saltcake, to be furnaced with coal; but they yield more glassy charges and require more reducing-coal than fresh charges. The crystals obtained from mother liquors alone are greenish, from fresh concentrated liquors brown, from less concentrated liquors yellow up to white. The commercial "anhydrous" sodium sulphide is obtained by melting the crystals in an iron pan at a moderate heat till the water of crystallization is driven out, then quickly crushing the mass and packing it in casks.

Very important improvements in the preparation of sodium sulphide have been introduced by Ellershausen (Engl. pat. 17815, 1890). He had found that the destructive action of sodium sulphide on the furnace is mostly caused by overheating the charge, which is hardly avoidable in ordinary open furnaces. It can, however, be remedied by making the fire-bridge very high, 2 feet above the furnace-bed, and avoiding overheating the bridge by means of an interior air-channel. The flue above the fire-bridge is contracted towards the furnace-bed, so that the flame is directed towards the central portion of the bed, and the sides do not get so hot as usual. The bed is also made to rise towards the bridge, so that no melted sodium sulphide can accumulate there. The sides of the furnace round the bed are made of fire-bricks in such manner that they are independent of the outer walls and are easily renewed.

To these statements, taken from the patent specification, we will add some personal observations made at a factory erected by Ellershausen. The charge consists of 7 cwt. saltcake and  $8\frac{1}{2}$  cwt. coke-breeze, not specially mixed, but put in the usual way first upon the back bed, and brought there to a dark red heat, without any fusion. The fusion takes place on the front bed, where the mass turns first thin, and then again thicker, just like an ordinary black-ash charge, but without exhibiting the well-known "candles." It is, however, not so pasty as black-ash and more porous. It is drawn out into an iron box, after first lowering the furnace-damper, to prevent its burning during the discharging. The mass cools down in these boxes without any special precautions.

Sixteen such charges are finished during 24 hours, with a consumption of  $1\frac{1}{2}$  tons of coal. The heat is not so high as in black-ash furnaces; the furnaces do not require much repair; and the whole style of working conveys the impression that Ellershausen had indeed completely overcome the difficulties of manufacturing sodium sulphide on a large scale, and that he worked quite as regularly as in ordinary black-ash making.

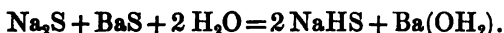
It is very remarkable that in this case the furnace-bottoms did not suffer very much, seeing that they were made exactly like those of black-ash furnaces (Vol. II. p. 507), except that they were a little sloping from the fire-bridge; the slope towards the working-door is common to both. The reason is probably this, that with the large quantity of small coke (50 per cent.) the mass always remains porous; the infusibility of coke is also an advantage in comparison with ordinary mixing-coal. During work the damper must be always kept down as much as possible, to avoid unnecessary entrance of air; if this is not done, the mass turns more liquid, evidently by the formation of polysulphides, and the furnace suffers much more. The crude sulphide on analysis shows only a trace of polysulphides, no sulphate at all, about  $1\frac{1}{2}$  per cent. thiosulphate, and about 10 per cent. of the soda as carbonate, the remaining soda being present as  $\text{Na}_2\text{S}$ ; there is about 25 per cent. insoluble. This is certainly an excellent product.

Gossage and Mathieson (Engl. pat. 3218, 1888) claimed to have found a considerable improvement in mixing the saltcake with a large quantity of common salt, which is to prevent the destructive action on the furnace-lining. They prefer to employ 100 saltcake, 50 coal, and 31 salt. This mixture is fused in an open furnace or a revolver; the mixture of sulphide and chloride thus obtained is drawn out into open vessels and cooled down there, without danger of oxidation, before being lixiviated. Each charge takes two or three hours, and is carried on just as in the Leblanc process. The solution is treated with sufficient  $\text{CO}_2$  to precipitate the soda as bicarbonate (see below).—This process has been tried for several years, but apparently without much advantage. The crude sulphide is stated to have tested: 31.1  $\text{Na}_2\text{S}$ ; 9.8  $\text{Na}_2\text{CO}_3$ ; 2.1  $\text{Na}_2\text{SO}_4$ ; 1.4  $\text{Na}_2\text{S}_2\text{O}_3$ ; 19.2  $\text{NaCl}$ ; 32.2 insoluble (coke).

The addition of salt could not have been found very useful, for

later on Gossage and Williamson (Engl. pat. 20921, 1892) proposed to add to the mixture of saltcake and coal 35 or 40 parts Leblanc waste, in order to prevent the action on the furnace-lining. Further patents of the same inventors (Nos. 22523 & 23616, 1892) describe the working-up of the sodium sulphide thus obtained into bicarbonate, almost precisely like the former patent of Mathieson and Hawliczek (*vide* p. 241).

Trachsel (Engl. pat. 3406, 1886) proceeds as follows:—A mixture of  $\text{Na}_2\text{SO}_4$  with  $\text{BaSO}_4$  (or  $\text{SrSO}_4$ ) and coal is furnaced and lixiviated. On cooling the solution, barium (or strontium) hydrate crystallizes out, and sodium sulphhydrate remains in solution :



This solution is treated with  $\text{CO}_2$ , and the  $\text{H}_2\text{S}$  is dealt with by well-known processes. [The  $\text{CO}_2$  will certainly act better on  $\text{NaHS}$  than on  $\text{Na}_2\text{S}$ , but the separation of the barium hydrate from the  $\text{NaHS}$  is anything but quantitative; we should also be informed how the baryta is to be utilized.]

Simpson (Engl. pat. 17765, 1890) employs nitre-cake or other acid sulphates, which are first neutralized with calcium sulphhydrate; the solution is filtered from the calcium sulphate and sulphur, and is completely decomposed by a further quantity of sulphhydrate, preferably in closed vessels under a pressure of 4 or 5 atmospheres, at which the  $\text{CaSO}_4$  is insoluble in the liquor. The  $\text{NaHS}$  is then carbonated with  $\text{CO}_2$ , and so forth.

Bong (Engl. pat. 895, 1879) reduces alkaline sulphates by  $\text{H}_2\text{S}$ , obtained in decomposing the  $\text{Na}_2\text{S}$  formed by  $\text{CO}_2$ , without any fusion.

Peitzsch (Engl. pat. 22569, 1894) patents the old process of reducing  $\text{Na}_2\text{SO}_4$  by carbon in closed vessels by outward heat at a low temperature. He employs thin iron vessels, not deeper than 4 inches, placed in horizontal or upright retorts [these will be very strongly acted upon !].

#### *Decomposition of Sodium Sulphide by Carbonic Acid.*

Gren had made the observation that an aqueous solution of sodium sulphide is converted into carbonate by carbonic-acid gas, with evolution of sulphuretted hydrogen if the introduction of

$\text{CO}_2$  is continued up to the formation of sodium bicarbonate. Attwood, on June 22, 1819, obtained an English patent for this process. Pelletan in 1829 made soda in a factory at Paris by this process; and Dumas explains it in detail in his treatise on applied chemistry, 1829. Gossage erroneously believed to have proved (in 1838) that  $\text{CO}_2$  decomposes its equivalent of  $\text{Na}_2\text{S}$  (comp. Vol. II. p. 612); and in 1861 he reverts to this in his 'History of the Soda Manufacture,' p. 22, stating that in future the  $\text{H}_2\text{S}$  would be absorbed by ferric oxide, and the product employed for making sulphuric acid. The working out of this idea (which he had failed to accomplish himself in the intervening twenty-three years!) he wished to leave to younger men. Endeavours in this direction have certainly not been wanting. Wagner quotes (Regesten, p. 37) patents taken out by Beringer (1847), Newton (1853), Hunt (1861), Reissig (1865). He thought that with the introduction of ferric oxide as an absorbent for sulphuretted hydrogen, this gas had ceased to be a source of inconvenience to the works and in their vicinity. We have seen how unfounded this opinion is (Vol. II. p. 883 *et seq.*). Even the utilization of comparatively concentrated  $\text{H}_2\text{S}$  was not satisfactorily achieved till twenty years later, and that of dilute gas, containing very varying quantities of  $\text{H}_2\text{S}$ , such as must have been formed in all former processes, is even now an open question, where the *economical* side has to be considered.

We shall first describe the decomposition of pure  $\text{Na}_2\text{S}$  in solution or in lumps, and then that of the crude products within the vessels where it has been prepared.

A great deal was expected in Lancashire of Hunt's patent (No. 1126, 1860). He asserted that he had found the decomposition of sodium sulphide to take place better than in solution, if the  $\text{Na}_2\text{S}$  was put, in pieces, on the perforated false bottoms of vessels, through which steam and  $\text{CO}_2$  (generated by igniting chalk in retorts) were conducted. By combining several vessels, the  $\text{CO}_2$  was to be completely spent and strong  $\text{H}_2\text{S}$  obtained, which was to be mixed with air, ignited, and employed for vitriol-making. This process was tried, among others, in the works of Mr. Shanks at St. Helens. The  $\text{CO}_2$  was there made from limestone and hydrochloric acid; and the  $\text{H}_2\text{S}$  was not dealt with at all, which sufficiently proves the experimental character of those trials. The peculiarity of Hunt's process, the treatment of

sodium sulphide in *lumps* with  $\text{CO}_2$ , is not essential: that even a *solution* of  $\text{Na}_2\text{S}$  is completely and comparatively easily decomposed by  $\text{CO}_2$ , I have myself seen at the works managed by Mr. Gibb; and the drawback observed there, that any oxygen remaining along with the  $\text{CO}_2$  caused the formation of thiosulphate and consequently a loss of available soda, must equally have occurred in Hunt's process.

Further patents upon this process, containing nothing essentially new, were taken out by Verstraet and Oliver (No. 2275, 1862: to the solution of  $\text{Na}_2\text{S}$  milk of lime is to be added in order to lessen the tendency to the formation of thiosulphates), Claus (No. 2616, 1869: he employs blast-furnace gases, along with the  $\text{CO}_2$  produced in reducing the  $\text{Na}_2\text{SO}_4$ ), Young (No. 2989, 1872: he employs a boiling solution of  $\text{Na}_2\text{S}$ ), Fletcher (No. 1786, 1873: he proposes employing the  $\text{SO}_2$ , generated by burning the  $\text{H}_2\text{S}$ , for Hargreaves' saltcake process), and Prache (1873: he, like many before him, conducts the  $\text{H}_2\text{S}$  into water in which hydrated ferric oxide is suspended, which is afterwards regenerated by exposure to the air; or the  $\text{CO}_2$  can be directly passed into a mixture of sodium sulphide and hydrated ferric oxide). Wallace and Claus (No. 2842, 1877) decompose alkaline sulphides by the gases escaping on saturating with acids the ammonia-liquor of gas-works (*i. e.* a mixture of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ ); thus pure  $\text{H}_2\text{S}$  is formed, which is burnt into  $\text{SO}_2$  or used for precipitating As, Cu, Ag, or Pb. Some other modifications are also described, but all of them founded upon the employment of gas-liquor; so that this, not the alkaline carbonates, is the principal consideration.

H. B. Condry (No. 1536, 1877) employs crystallized sodium sulphide with 67 per cent. water, which is treated with  $\text{CO}_2$  in a closed space on a perforated bottom; by the liquefaction of the water of crystallization a solution of sodium carbonate and bicarbonate is formed; the  $\text{H}_2\text{S}$  is absorbed or burnt according to any one of the known plans.

In Weldon's patents mentioned on p. 229 the treatment of the sodium sulphide is described as follows:—The sodium sulphide may be mixed with silica or alumina in the state of powder and decomposed by superheated steam in the cylinder furnace itself or in another furnace, during which time the other end of the furnace must be connected with the apparatus for burning or absorbing the sulphuretted hydrogen, after cooling and condensing the

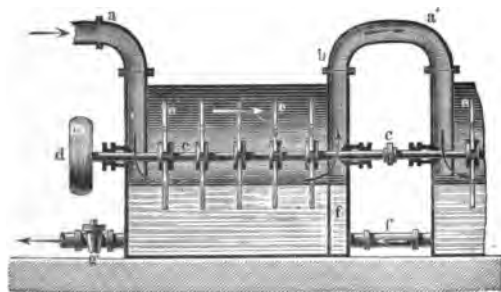
water; sodium silicate or aluminate remains behind. [This part of the process does not seem to have been seriously carried out on a large scale.] Or else the sodium sulphide is treated with carbonic acid in the following way:—The sulphide is run into airtight iron boxes lined with coal, and after sufficient cooling lixivated with exclusion of air. The liquor is made so strong as to contain at least 12 per cent.  $\text{Na}_2\text{S}$ ; but it is better to make it quite saturated, so as to contain 17 to 20 per cent.  $\text{Na}_2\text{S}$ . The solution is then treated with carbonic acid in a methodical way, in a set of six closed vessels. The liquor only half fills these vessels; and by a mechanical agitator their upper halves are constantly filled with a spray; there are also several partitions reaching down from the cover nearly to the level of the liquid, so as to force the gases to travel in a circuitous route. By means of a suitable system of cocks and pipes, gas can be admitted into the upper part of each vessel, and conveyed through all the other vessels in succession. In this way the complete decomposition of the sodium-sulphide liquor in the first vessel can be attained, and at the same time the gas issuing from the sixth vessel consists of practically pure sulphuretted hydrogen. When the liquor of the first vessel is sufficiently decomposed, it is run off, fresh liquor is run in, and the second vessel is now made the first, the sixth fifth, the first sixth with respect to the current of gas, and so forth. Instead of this the gas may also be passed through the vessels always in the same succession; but then the liquors, after completing the decomposition, are run from one vessel into the other in the opposite direction. This, however, can only be done if the decomposition is not carried so far as to precipitate bicarbonate in a solid form. Usually the operation is so conducted as to obtain as large a separation of crystals as possible, and, for this reason, at the ordinary or only a slightly raised temperature, both of the liquor and of the carbonic acid. In this way up to 80 per cent. of the soda can be obtained as a precipitate of bicarbonate; the impurities consequently remain in the mother liquor, which is washed off with a cold saturated solution of bicarbonate, whereupon the residue is brought into saleable form either as bicarbonate or as alkali. The mother liquor is again employed for dissolving sodium sulphide, till it has become too much charged with impurities. It is much better not to carry on the operation till all the sodium sulphide is decomposed, because this can only



be done by a large excess of carbonic acid; the mother liquor containing sodium sulphide can be easily employed for dissolving a fresh batch. The treatment is accordingly only continued till at least 50 or at most 80 per cent. of the sodium sulphide has been decomposed. If the treatment does not take place in the cold, but at a higher temperature, instead of bicarbonate sesquicarbonate is obtained, which on the cooling of the liquid crystallizes out. If the sulphide contains polysulphides, it is necessary to work with dilute liquors, so that the sulphur can settle down.

The construction of the absorbing vessels is more clearly shown by the section, fig. 87: *a a'* are entrance-pipes for the gases,

Fig. 87.



reaching down nearly to the surface of the liquid and nicked out at the bottom; *b*, exit-pipe; *c*, a shaft revolving in glands above the liquid, driven by the pulley *d*, and carrying the agitating-blades *ee*; *f*, connecting-pipe for the liquid; *g*, running-off cock for the same. The vessels may be made of iron, covered with hard pitch, or of hard wood, if the sodium-sulphide liquor is to be treated cold, but of iron covered with lead or stone flags if at a higher temperature. Similarly the agitating-shaft is protected from the effect of the sulphide by a coating of pitch or iron. The agitating-paddles best consist of hard wood.

It remains to deal with the sulphuretted hydrogen gas which is given off on the treatment of the  $\text{Na}_2\text{S}$  in the furnace itself with superheated steam, or on that of its solution with  $\text{CO}_2$ . For this the process patented by Weldon as No. 2008, 1871, is to be employed. It consists in bringing the gas into contact with a metallic oxide suspended in water, hydrated ferric oxide being the best (compare also Lunge's patent, No. 1108, 1866). This treat-

ment is to take place in an apparatus quite similar to that serving for the introduction of  $\text{CO}_2$ ; so that the gas is introduced on the top of the first of six vessels in which the metallic oxide suspended in water is constantly splashed about by a paddle-wheel, and escapes out of the sixth vessel completely deprived of its  $\text{H}_2\text{S}$ . When the metallic oxide in the first vessel is entirely converted into a sulphide or a mixture of a sulphide with sulphur, the contents of the vessel are drawn off, those of the second vessel are run into the first, those of the third into the second, and so forth; the sixth vessel, which gets emptied, is charged with a fresh mixture of oxide and water. The mixture run off from the first vessel and saturated with  $\text{H}_2\text{S}$  is treated with a strong current of air in an oxidizing-tower similar to those used in Weldon's manganese-recovery process; this converts it into a mixture of hydrated ferric oxide and sulphur, suspended in water, which can be employed directly in the absorbing-vessels; but when it has become very rich in sulphur, this must be kept separate, and either, by dissolving the iron in  $\text{HCl}$ , the sulphur obtained as such, or the whole must be dried and the sulphur burnt.

These processes were carried out on a rather large scale by a company founded for this purpose, but, in spite of all exertions, have now been given up as impracticable. The reason stated for this is that pure sodium sulphide, entirely free from polysulphides, thiosulphates, and caustic, such as was recovered in Weldon's furnace, turned out entirely infusible and could not be got out of the furnace; if, on the other hand, some air was admitted in order to form a little of those compounds and thus to make the mass fusible, the carbon lining of the furnace was quickly burnt and repairs were constantly required. [We have seen, p. 231 *et seq.*, that the preparation of the sodium sulphide itself would hardly form an unsurmountable obstacle to the success of this process.]

J. B. Thompson (Engl. pat. 10900, 1887) describes the same process as Weldon; his apparatus consists of a long boiler with horizontal shaft, on which blades are arranged in the shape of a screw, which half dip in the liquid, and cause the gas to come into intimate contact therewith.

A. M. and J. F. Chance (Engl. pat. 1495, 1888) apply to the decomposition of  $\text{Na}_2\text{S}$  the same principle as to that of  $\text{CaS}$  from Leblanc waste (Vol. II. p. 869), that is, removing part of the nitrogen, in order to obtain more concentrated  $\text{H}_2\text{S}$ .

Wallis (Engl. pat. 15367, 1888) applies the treatment with  $\text{CO}_2$  to  $\text{Na}_2\text{S}$  obtained as a slag at lead-works.

Parnell and Simpson (Engl. pat. 19023, 1888) describe an apparatus with nine compartments, in which  $\text{Na}_2\text{S}$  solution is systematically treated on Chance's principle.

Mathieson and Hawliczek (Engl. pat. 227, 1886) apply the process already described Vol. II. p. 614, in connection with Leblanc crude liquors, to sodium sulphide (comp. its preparation, p. 234). They dissolve the crude sodium sulphide in brine containing 16 to 19 per cent.  $\text{NaCl}$ , and pass  $\text{CO}_2$  through it in tall cylindrical vessels, provided with perforated false bottoms for dividing the gas. At first the impurities are precipitated—alumina, silica, and ferric oxide—and are removed by filtration; afterwards sodium bicarbonate is precipitated at  $26^\circ$  to  $30^\circ \text{C.}$ , and is separated from the mother liquor by a centrifugal machine, &c. It is pure enough to be sold as such, but it can be, of course, converted into soda-ash by calcining. Gossage and Williamson apply precisely the same method to the sodium sulphide manufactured by their own process (Engl. pat. 22523 & 23616, 1892; comp. p. 235).

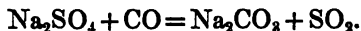
*Decomposition of Sodium Sulphide in the same vessels in which it has been prepared.*

Laming (Prov. Protection, No. 1367, 1861) heats a mixture of saltcake and coal, and afterwards passes a current of steam and air through it, until no more  $\text{H}_2\text{S}$  escapes, whereupon the sodium carbonate is obtained from the residue by lixiviation. [Evidently the air must form  $\text{CO}_2$  with the excess of coal present.]

Vogt and Figge (Germ. pat. 31675) mix saltcake with clay, magnesia, lime, or silica, and convert the mixture by heating into a porous mass, not fusible at a red heat. This is broken up, and is exposed to a current of carbon monoxide passing downwards in perpendicular iron retorts. Thus the sulphate is converted into sulphide [this can certainly be accomplished by  $\text{CO}$  alone, as shown by my experiments, Vol. II. p. 19]. The  $\text{CO}_2$  escaping here is utilized for converting the sulphide into carbonate, by forcing it, together with water, through the retort by means of an injector connected with the bottom of the retort, until all the sulphur has been driven off as  $\text{H}_2\text{S}$ .

Kayser, Young, and Williams (Engl. pat. 7355, 1885) claim

to have discovered that sodium sulphate, exposed at a dark red heat to a mixture of equal molecules of CO and CO<sub>2</sub>, is converted into carbonate, whilst SO<sub>2</sub> escapes, which can be used for preparing Na<sub>2</sub>SO<sub>4</sub> by the Hargreaves process (Vol. II.). In the same set of cylinders first NaCl is transformed into Na<sub>2</sub>SO<sub>4</sub>, and this afterwards into Na<sub>2</sub>CO<sub>3</sub>, without employing anything else than CO and CO<sub>2</sub>. The principal reaction would be :



The CO<sub>2</sub> would take no part in the reaction, and would only serve for preventing the formation of Na<sub>2</sub>S.

Watson Smith and Hart (Journ. Soc. Chem. Ind. 1886, p. 643) have examined this process in the laboratory, but with very unsatisfactory results. At a dark-red heat no reaction sets in even in the presence of moisture. At a bright-red heat and in the presence of moisture, CO reduces the Na<sub>2</sub>SO<sub>4</sub> to Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S. No SO<sub>2</sub> escaped at any time, only H<sub>2</sub>S; the reaction hence never went beyond the stage of Na<sub>2</sub>S, but even this quite incompletely : Na<sub>2</sub>CO<sub>3</sub> was never found. If no steam was employed, and rather more than 1 mol. CO<sub>2</sub> was present to 1 mol. CO, no reduction of the Na<sub>2</sub>SO<sub>4</sub> took place.

It is, however, probable that better results than the above can be obtained under other circumstances, for the Hautmont Chemical Works have tried the process on a large scale for several years, as I have explained in my Report on the Paris Exhibition (Zsch. f. angew. Chem. 1889, p. 601). Considerable mechanical difficulties arose by the crumbling of the lumps and in keeping the proper temperature: the reaction only begins at 550° C., and cannot be continued beyond 650°, owing to the softening of the sulphide. The best results were obtained when working very slowly, that is extending the time of conversion to ten or twelve days, with cylinders 5 ft. diameter and 6 ft. 6 in. high, holding 2 tons of saltcake in the shape of Hargreaves cakes. In this case the composition of the product was : 96·2 Na<sub>2</sub>CO<sub>3</sub>, 1·7 Na<sub>2</sub>SO<sub>4</sub>, 0·2 Na<sub>2</sub>S, 0·1 NaCl, 1·8 insoluble. No utilization of the SO<sub>2</sub> was attempted. [I pointed out at the same time that this analysis evidently referred to picked lumps, not to a real average sample, and that the great dilution of the SO<sub>2</sub> with CO<sub>2</sub> and N makes it perfectly hopeless to think of utilizing it for the manufacture of sulphuric acid or for the Hargreaves process.]

Claus (Engl. pat. 4922, 1886) charges a Hargreaves apparatus with a mixture of common salt and small coal, and converts it into saltcake in the ordinary way, or by burning  $\text{H}_2\text{S}$  recovered from Leblanc waste. The resulting mixture of  $\text{Na}_2\text{SO}_4$  and coke is brought to a higher temperature by heating the cylinders, and heated water-gas (that is a mixture of  $\text{CO}$  and  $\text{H}$ ) is passed through, thus reducing the sulphate to sulphide. Now a mixture of  $\text{CO}_2$  and steam (obtained by the action of the water-gas on the sulphate) is passed through; the  $\text{H}_2\text{S}$  escaping is burned, and the product is employed as above; the residue is separated by lixiviation into a solution of sodium carbonate and coke, which is again mixed with salt, and so on.

Quite similar to this process is that of G. E. Davis (Engl. pat. 11846, 1887). He also employs water-gas for reducing saltcake, obtained in a Hargreaves apparatus, but without any admixture of coke. According to him only the hydrogen has a reducing action, and the  $\text{CO}$  escapes unchanged with the excess of hydrogen and the steam formed in the reaction. These gases are to be passed over heated surfaces, by which they are transformed into  $\text{CO}_2$  and  $\text{H}$ . The  $\text{CO}_2$  is then employed for decomposing the sodium sulphide.

Long before this A. E. Fletcher had obtained provisional protection (No. 1786, 1873) for transforming  $\text{NaCl}$  by  $\text{SO}_2$ , steam, and air into  $\text{Na}_2\text{SO}_4$ , treatment of the latter with reducing gases in the same vessels, and conversion of the  $\text{Na}_2\text{S}$  thus formed into carbonate by  $\text{CO}_2$ .

*Action of calcium sulphydrate on sodium sulphate.*—We have already (Vol. II. p. 867) briefly mentioned the process of Haddock and Leith (Engl. pat. 11296 & 15648, 1890; paper by Leith in Journ. Soc. Chem. Ind. 1890, p. 214). This combines the Leblanc process with a new one, utilizing the  $\text{CaS}$  waste of the former by treating it with  $\text{H}_2\text{S}$  after mixing it with water to a paste, and thus converting the  $\text{CaS}$  into soluble sulphydrate,  $\text{CaS}_2\text{H}_2$ . The solution of the latter is treated with a strong solution of sodium sulphate, thus forming a precipitate of calcium sulphate and a solution of sodium sulphydrate. The latter is converted into bicarbonate by passing  $\text{CO}_2$  through it; half of the escaping  $\text{H}_2\text{S}$  is employed for treating a fresh quantity of Leblanc waste; the other half remains at disposal for the various purposes of utilization, described Vol. II. p. 883 *et seq.* Thus of a given

quantity of saltcake always one half is worked up by the Leblanc process, and the other half is treated by the new process, by means of the  $\text{CaS}_2\text{H}_2$  obtained from the waste of the former. Half of the sulphur is obtained as calcium sulphate ("pearl-hardening"), the other half as  $\text{H}_2\text{S}$ . Great hopes were entertained that all this pearl-hardening might be utilized in the manufacture of paper and textile fabrics.

The sodium sulphate is to be dissolved in the washings of the process, adding the mother liquor from the bicarbonate, thus saturating the free acid and precipitating the iron, lime, and magnesia contained in ordinary saltcake. The clarified solution is mixed with an equally clarified solution of calcium sulphhydrate, and the mixture conveyed to a filter, where the  $\text{CaSO}_4$  is retained. The solution of  $\text{NaHS}$  running off is freed from dissolved  $\text{CaSO}_4$  by adding some bicarbonate liquor, and after filtration is concentrated in vacuum pans until it contains 26.2 per cent.  $\text{NaHS}$  = 14.5 per cent.  $\text{Na}_2\text{O}$ . It is now treated in Solvay towers or similar apparatus with  $\text{CO}_2$ , free from oxygen, until its alkalinity is reduced to 3.4 per cent.  $\text{Na}_2\text{O}$  or below. The precipitate of sodium bicarbonate is filtered, washed, and dried or calcined; the escaping  $\text{CO}_2$  is used over again. As before mentioned, part of the  $\text{H}_2\text{S}$  formed in this operation is used again in the process and part is utilized in other ways. The bicarbonate mother liquors are again treated with  $\text{CO}_2$ , to precipitate more  $\text{NaHCO}_3$ , and the new mother liquors are employed for dissolving fresh saltcake.

The treatment of the Leblanc waste by 30 per cent.  $\text{H}_2\text{S}$  takes place in a set of four "carbonators," upright cylinders with hemispherical ends, just as in the Claus-Chance process (Vol. II. p. 872); it takes about four or five hours. With a 50 ton set this quantity can be treated every 24 hours. About 1 per cent. sulphur (equal to 8 per cent. of the total sulphur) remains in the mass, about  $\frac{1}{2}$  to  $\frac{3}{4}$  per cent. as ferrous sulphide, that is as an unavoidable loss. Even with 15 per cent.  $\text{H}_2\text{S}$  solutions are obtained containing 14 per cent. soluble sulphur, and with stronger gas up to 18 per cent. soluble sulphur can be obtained.

Leith quotes calculations, according to which the manufacture of a ton of 58 per cent. soda-ash leaves a profit of £6 5s., assuming the value of the pearl-hardening = £3 4s. (£2 per ton, present market price £3 5s.); the recovered sulphur, &c., is also taken into account. He points out many advantages of the process,

especially the preparation of NaHS in the wet way, the fact that no ammonia is required and that the bicarbonate need not be purified from it, the absence of any waste, and so forth.

During the discussion of the paper (*loc. cit.* p. 219) these claims for improvements were strongly attacked; especially doubts were raised concerning the purity of the precipitated calcium sulphate and the possibility of disposing of such large quantities of it; Hurter objected to nearly all the figures given by Leith and to the possibility of manufacturing soda-ash of the degree of purity claimed.

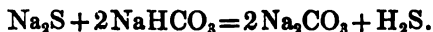
The process of Haddock and Leith undoubtedly possesses some great theoretical advantages; but the reactions will hardly be effected so easily as anticipated, and the realization of the profits depends entirely on the very doubtful utilization of by-products. In spite of the enormous profit shown by calculation, it does not seem to have been carried out on the large scale.

*Decomposition of Sodium Sulphide in other ways than by gaseous carbonic acid.*

*By acetic acid.*—Sodium sulphide obtained by heating sulphate with coal, according to Duhamel and Marggraf, is converted into acetate, and this by drying and ignition into carbonate. This process is only of historical interest.

*By steam.*—Gossage (Prov. Prot. 1176, 1870) proposed superheated steam for decomposing  $\text{Na}_2\text{S}$  into  $\text{NaOH}$  and  $\text{H}_2\text{S}$ , but did not complete the patent.

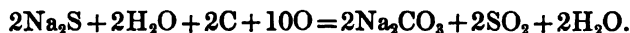
*By sodium bicarbonate.*—Wilson (No. 8399, 1840) patented the decomposition of sodium sulphide and bicarbonate into monocarbonate and sulphuretted hydrogen, thus:



A solution of 48 parts sodium sulphide is to be boiled with 85 parts dry sodium bicarbonate, the  $\text{H}_2\text{S}$  collected in a gas-holder and burnt in order to be converted into sulphuric acid in vitriol-chambers. Werckshagen patented the same process (No. 321, 1853); he proposes to make sulphur from the  $\text{H}_2\text{S}$  by bringing it into contact with  $\text{SO}_2$  and steam. Böhringer and Clemm (No. 945, 1853) again patented the same thing, also with the proposal to decompose  $\text{H}_2\text{S}$  by  $\text{SO}_2$ . Both Wilson and Gossage include this process in their patents of 1858 (see above).

We have seen (Vol. II. p. 612) that all these processes rest on a wrong basis. The reaction between  $\text{Na}_2\text{S}$  and  $\text{NaHCO}_3$  is quite incomplete and cannot possibly be carried out in the above way. The decomposition requires a large excess of  $\text{CO}_2$ , which renders the utilization of the  $\text{H}_2\text{S}$  too difficult.

*By heating with coal.*—Pedder (Engl. pat. 2373, 1894) heats 55 parts of sodium sulphate with 48 parts of coal. The product, consisting of sodium sulphide and carbon, is ground up with carbon and water, and heated in a revolving furnace, so as either to volatilize [?] or to oxidize the sulphur. In the latter case the reaction is stated to be:



*By caustic soda or caustic lime.*—Tessié du Motay (No. 1746, 1870) proposes these for decomposing sodium sulphide by heating them together.

*By ammonium carbonate.*—Laming (patent No. 2607, 1859) proposed a number of different ways for making sodium carbonate from sulphide by means of ammoniacal gas-liquor. The principal being in all the same, it will suffice to describe one of these plans. Sodium sulphide is moistened with strong ammoniacal liquor (*i. e.* mostly ammonium carbonate and sulphhydrate), and heated to dryness in a retort at a temperature of  $150^\circ\text{C}$ .; ammonium sulphhydrate volatilizes; and from the residue in the retort sodium carbonate is extracted by lixiviation. The ammonium sulphhydrate is conducted through a porous mass containing hydrated iron oxide; here it issues as  $\text{H}_2\text{S}$ ; and pure  $\text{NH}_3$  escapes, which by treatment with carbonic-acid gas is reconverted into ammonium carbonate.

*By magnesium carbonate, &c.*—Clemm (French patent, Oct. 6th, 1853) proposes mixing a concentrated solution of sodium sulphide with neutral magnesium carbonate and heating to  $300^\circ\text{C}$ . Or 1 equivalent of common salt is decomposed by 2 equivalents of kieserite (anhydrous magnesium sulphate); by this a double sodium magnesium sulphate is formed, mixed with  $\text{MgCl}_2$ : this is evaporated to dryness, ignited till the latter has been decomposed into  $\text{MgO}$  and  $\text{HCl}$ , 25 to 30 per cent. coal added to the residual mixture of the double salt and magnesia, and the mass heated on a hearth made of magnesite. Hereby  $\text{SO}_2$  escapes and is worked for vitriol. The porous mass is allowed to cool in closed vessels;



it contains sodium sulphide, magnesia, soda, and an excess of coal. It is treated with  $\text{CO}_2$  in order to expel the  $\text{H}_2\text{S}$ , and at last heated to  $300^\circ \text{C}$ . in order to drive off all the sulphur.

*By native carbonate of iron.*—Habich (Dingl. Journ. cxl. p. 370) proposed this method at first for desulphurizing ordinary black-ash tank-liquor, and afterwards as a soda-making process. But, according to the unanimous testimony of practical men, that mineral can effect neither the one purpose nor the other, as it acts too slowly and incompletely. The same process had been already patented in England by Cottrill (No. 74, 1853). In France, De la Souchère patented it again in 1878.

*By alumina.*—Wagner (in his 'Jahresbericht,' 1865, p. 332) proposes to employ, instead of carbon dioxide, the much more active alumina (from bauxite or cryolite) for expelling the sulphur from  $\text{Na}_2\text{S}$ , by boiling it with a solution of the latter. The  $\text{H}_2\text{S}$  is to be absorbed by Laming's mixture or ferric chloride, and the sodium aluminate converted by  $\text{CO}_2$  into carbonate and aluminium hydrate. This method seems never to have been tried anywhere. If the alumina really acted simply and easily, it would also furnish pure  $\text{H}_2\text{S}$ ; but it does not look very promising.

A modification of this process was patented by Siermann (German patent, No. 3280, 1878). Sodium sulphate and alumina are ground up together, leaving a slight excess of the former, and heated in an iron muffle completely surrounded by fire, allowing the air to enter as soon as the mass has attained a bright-red heat. Sulphur dioxide is given off and collected in a chamber common to several muffles, which are charged alternately so as to produce a uniform current of  $\text{SO}_2$ , which is conveyed into vitriol-chambers. The residue in the muffle, consisting of sodium aluminate, is drawn out, lixiviated with water, and carbon dioxide passed through the solution till it has been decomposed into a precipitate of aluminium hydrate and a solution of sodium carbonate. The former is used over again in the first part of the process. The carbon dioxide is best supplied by the fire-gases from the muffle-fire, which is for this purpose fed with coke.—This process is anything but a cheap one: the sodium sulphide will play great havoc with the iron muffles; and the gas evolved can hardly be converted into sulphuric acid with any pecuniary profit.

*By ferric or manganic oxide in the wet way.*—Arrott (No. 1370, 1859) patented the following process:—A quantity of peroxide

of iron or oxide of manganese is put into a solution of caustic soda, and the solution is evaporated and heated until the whole has assumed an olive-yellow colour. Water dissolves out from this mass caustic soda, leaving the oxide in a state to take sulphur from the sodium sulphide. A solution of this is now added so long as the oxide continues to take up sulphur, whereby a solution of caustic soda and a precipitate of  $\text{FeS}$  or  $\text{MnS}$  is produced. The weight of the metallic oxide must at least equal that of the  $\text{Na}_2\text{S}$ . The oxide, caustic soda, and solution of sodium sulphide may be added together. Caustic soda is obtained by heating carbonate of soda and peroxide of iron or manganese together to a full red heat for two or three hours and lixiviating the residue.

Gossage (No. 2612, 1859) mixes a solution of sodium sulphide with ferric oxide, and injects a current of carbonic acid by means of a forcing-pump; or he decomposes sodium sulphide by sodium bicarbonate or sesquicarbonate in the presence of ferric oxide. Iron sulphide is precipitated, which is either dried and burned for the production of sulphuric acid, or fluxed with common salt with access of air to form sulphate.

Wilson (No. 7879, 1838) treats a solution of sodium sulphide with hydrated iron protoxide, and passes steam through the mixture. The  $\text{Fe}(\text{OH})_2$  is obtained by precipitating  $\text{FeCl}_2$  with milk of lime, the  $\text{FeCl}_2$  by boiling copperas solution with common salt, in which case anhydrous sodium sulphate is precipitated. The copperas is recovered by treating the  $\text{FeS}$  with sulphuric acid, burning the  $\text{H}_2\text{S}$ , and making from it sulphuric acid again (!).

The sodium sulphide-ferric oxide process, after being neglected for a long time, was again brought in to notice by the labours of Ellershausen (Engl. pat. 1015, 9112, 16676 & 17815, all of 1890). The following description is principally based upon my personal observations at the works erected by the inventor (p. 233) and on my own analyses of the products. His improvements start from the production of the sodium sulphide, as explained on p. 233. The sodium sulphide is dissolved in any suitable apparatus, first with weak liquor of a former operation, then with water, the temperature being kept at about  $40^\circ \text{C}$ . by the chemical reaction itself. The lixiviation is stopped when the solution turns yellow; this is supposed to show that the more easily soluble  $\text{Na}_2\text{S}$  is exhausted, and that new polysulphides,

mostly formed during the dissolving process, enter into solution. The specific gravity of the liquor should not exceed 1.18. An analysis made by myself showed no polysulphides, but 3 grms. of sulphur per litre as thiosulphate, 0.77 gm. S as sulphate, and 71 grms. S as  $\text{Na}_2\text{S}$ : altogether this corresponds to 144 grms.  $\text{Na}_2\text{O}$ , to which must be added 8.75 grms.  $\text{Na}_2\text{O}$  as carbonate and 2.4 as chloride. Other analyses (by Netto) of such solutions showed 14 to 20 p. c.  $\text{Na}_2\text{O}$  as sulphide, 0.3 to 1.3 p. c. as thiosulphate, 0.8 to 2.5 p. c. as sulphate, 1.0 to 3.4 p. c. as carbonate (all calculated as gm. per cent. in 100 cub. cent. of liquor).

The weight of the insoluble residue is about 10 p. c. of the crude sulphate; it contains about 60 or 70 p. c. coke, 4 p. c. sulphur (3 p. c. not yet fully oxidized), and over 15 p. c.  $\text{Na}_2\text{O}$ , mostly in an insoluble state.

Probably it might be used over again for reducing saltcake to sulphide, until the mineral matter of the coke accumulated too much. When thrown upon a heap, it becomes heated under the influence of the air, but it emits no smell of  $\text{H}_2\text{S}$ , and after being sufficiently weathered it yields on lixiviation a good crop of commercial sodium thiosulphate (hyposulphite). On an average it then contains 12 p. c. of this salt and 2 p. c. of  $\text{Na}_2\text{SO}_4$ , and the residue from its lixiviation, which contains about 7 p. c. insoluble  $\text{Na}_2\text{O}$ , is perfectly harmless.

The principal novelty in Ellershausen's process is this: that he causes the sodium sulphide to react not with ferric oxide, which acts too slowly, but in a much more rapid and complete manner with *sodium ferrite*,  $\text{Na}_2\text{O}, \text{Fe}_2\text{O}_3$ , formed by heating soda-ash with ferric oxide, with evolution of  $\text{CO}_2$ . It is practically made by heating "purple ore" from the wet copper-extraction process (Vol. I. p. 808) with some cheap kind of soda-ash, of which much less is taken than corresponds to the above formula, viz. only so much that for each 100 parts of crude purple ore 25 parts of  $\text{Na}_2\text{O} = 40$  parts of good soda-ash are employed. The heating takes place in an ordinary open calciner, which is kept at a pretty good heat, and in 24 hours consumes 30 cwt. of coal. During this time 8 batches of 10 cwt. purple ore with the corresponding quantity of soda are put through. The product contains about 70 p. c.  $\text{Fe}_2\text{O}_3$  and 15 to 20 p. c.  $\text{Na}_2\text{O}$ ; also about 5 p. c.  $\text{Na}_2\text{CO}_3$  and 5 p. c.  $\text{Na}_2\text{SO}_4$ . (The formula  $\text{Na}_2\text{CO}_3$  requires 27  $\text{Na}_2\text{O}$  to 70  $\text{Fe}_2\text{O}_3$ .)

It is well known that sodium ferrite is decomposed by hot water

into ferric oxide and sodium hydrate; but in the Ellershausen process it is employed in the granular state, quite hot as it comes from the furnace (this is important to observe!), and is brought into methodical contact with  $\text{Na}_2\text{S}$  by filtering the solution of the latter first through partially spent and then through fresh sodium ferrite, by which treatment the  $\text{Na}_2\text{S}$  is almost completely transformed into  $\text{NaOH}$ . This reaction is, however, somewhat complicated, by the formation of a ferrosodium sulphide to which Ellershausen gives the formula  $\text{Fe}_2\text{Na}_2\text{S}_4$ . This would correspond to the following reaction:—



Probably several ferrosodium sulphides of different composition are formed, but all of these are insoluble and do not carry any iron into the solution, whereas the ferrosodium sulphides occurring in the Leblanc process are soluble (Vol. II. p. 603).

In the Ellershausen process the formation of soluble compounds of this kind can only be avoided by not allowing the liquors to exceed spec. grav. 1.18; otherwise iron is found in the liquor. This also occurs through contact with air, and is proved by the brown colour of the liquors.

The filtration takes place through a layer of sodium ferrite, from 18 inches to 3 feet thick, resting on a bed of coke. The spent ferrite contains 10 p. c.  $\text{Na}_2\text{S}$ , 37 p. c.  $\text{Fe}_2\text{S}_3$ , 19 p. c.  $\text{Fe}_2\text{O}_3$ , 28 p. c.  $\text{H}_2\text{O}$ , &c. Its treatment will be described later on. The caustic liquor running off is more concentrated than would be expected, viz. spec. grav. 1.275, possibly because the newly formed insoluble compounds absorb some water for the formation of hydrates. Analyses of the caustic liquor show 11 to 30 p. c.  $\text{NaOH}$ , 4 to 10 p. c.  $\text{Na}_2\text{CO}_3$ , 4 to 6 p. c.  $\text{Na}_2\text{SO}_4$  (after oxidizing the total sulphur); there is very little unchanged sulphide present. This liquor is sufficiently concentrated to be at once charged into a caustic pot (Vol. II. p. 786); here it is brought to spec. grav. 1.55, settled for 12 hours, and finished in a second pot. The first concentration takes two days, the second a whole week. Each pot, containing 14 tons of caustic, receives 5 cwt. of nitrate of soda, when the spec. gravity of the liquor has risen to 1.45. Each pot furnishes 13 tons best white caustic and 1 ton bottoms of a grey colour.

A difficulty in the Ellershausen process consists in the treatment

of the "spent ferrite." According to his patent No. 16676, 1890, it should either be decomposed by roasting into ferric oxide, sodium sulphate, and  $\text{SO}_2$ , or it should be exposed to the action of the air, in order to lixiviate the sodium thiosulphate and to obtain ferrous sulphide, which is to be utilized by burning. Neither of these processes is practicable, owing partly to the want of utilization for the soda, and partly to the impossibility of treating economically such dilute  $\text{SO}_2$  as must be formed here.

Undoubtedly the Ellershausen process has several important advantages in comparison with the Leblanc process. It furnishes direct from sodium sulphide a rather concentrated solution of caustic soda, without employing calcium carbonate for producing "black-ash," or quicklime for causticizing; there is also no waste of an offensive character. But its great drawback is the retention of all the sulphur and of very much soda (theoretically  $\frac{1}{2}$  of the whole, practically of course more) in the "spent ferrite." According to a later patent (No. 20012, 1890) Ellershausen proposes to decompose this by carbonic acid, either in the wet state, with formation of  $\text{H}_2\text{S}$ , or in the dry state in a muffle-furnace, with formation of  $\text{SO}_2$ : the residual mixture of sodium carbonate and ferric oxide was to be re-converted into sodium ferrite by heating in a furnace. The second of these alternatives is impossible, as the sodium will not be transformed into carbonate, but principally into sulphate, and the  $\text{SO}_2$  certainly cannot be utilized. Neither is the first practicable, since the decomposition of the insoluble ferrosodium sulphides by  $\text{CO}_2$  is quite incomplete. This decomposition is much more complete in the process patented by Lunge and Dewar (No. 8018, 1891), viz. the simultaneous action of 1 vol.  $\text{CO}_2$  and 4 vols. atmospheric air on the substance in a moist state. In this case most of the soda is converted into carbonate, very little of it into thiosulphate, and both are removed by lixiviation. The residue besides ferric hydroxide contains very much free sulphur, which can be obtained by melting, burning, or extracting with carbon sulphide; also a little soda in the shape of another ferrosodium sulphide, which is utilized by mixing the washed residue with more soda-ash and working it again for sodium ferrite. This process, however, has not been carried out beyond the laboratory, as the Ellershausen process had in the meantime ceased to work on a manufacturing scale.

*By copper, zinc, or lead oxide.*—As early as 1804 Clayfield

obtained a patent (No. 2793) for treating sodium sulphide with lead or zinc, or their oxides, for the purpose of alkali-making. Prückner in 1829 gained a prize offered by the St. Petersburg Academy of Sciences for the following process :—Sodium chloride with ammonium sulphate are decomposed into sodium sulphate and ammonium chloride. By ignition with coal the sulphate is reduced to sulphide; and its solution is boiled with coppersmiths' scales ( $\text{Cu}_2\text{O}$ ) till all the sulphur has been precipitated as copper sulphide and only caustic soda remains. The former, by gentle roasting, is converted into cupric sulphate, or more strongly heated till only  $\text{CuO}$  remains; the escaping  $\text{SO}_2$  is conducted into ammonia-liquor, obtained by heating the ammonium chloride of the first operation with lime. The ammonium sulphite remains in contact with the air till it has been converted into sulphate, and can serve for again decomposing common salt. The caustic soda is used as such, or, by evaporating with coal-dust and igniting, converted into carbonate (!). In 1839, Poole, for some anonymous individual, obtained a patent (No. 8304) for an exactly similar process; but he converts his caustic in a more rational way into carbonate (if such a conversion can be called rational at all), viz., by a current of  $\text{CO}_2$  in a tower filled with pieces of granite. The ammonium sulphite is oxidized by exposing its solution for a sufficient time to a current of air in a vessel filled with wood shavings, analogous to a vinegar-making tub. Shortly after (No. 8356, 1840) Hunt patented the same method in a somewhat different form. Sodium sulphide, obtained by heating sulphate with one-third of coals, is dissolved and treated with a mixture of  $20\text{Cu}_2\text{O}$  (obtained by decomposing  $\text{Cu}_2\text{Cl}_2$  with lime) and 1 metallic copper, so that caustic soda and copper sulphide are formed. The latter is gently heated in order to obtain cupric sulphate, which is decomposed with  $\text{NaCl}$  into  $\text{CuCl}_2$  and  $\text{Na}_2\text{SO}_4$ ; the  $\text{CuCl}_2$  being digested with finely divided copper, is converted into  $\text{Cu}_2\text{Cl}_2$ , which, owing to its insolubility, is easily separated from the solution of sodium sulphate. Instead of  $\text{CuO}$ ,  $\text{ZnO}$  may be employed for desulphurizing. The metallic sulphides may also be more strongly roasted, and the arising  $\text{SO}_2$  utilized in vitriol-chambers.

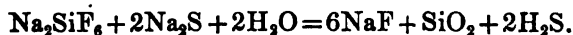
Possoz (Compt. Rend. xlvii. p. 848) takes up the proposal of Prückner (also advocated by Persoz), principally in order to employ the caustic soda for making oxalic acid from sawdust according to his method. Possoz found that the suboxide,  $\text{Cu}_4\text{O}$ ,

is more suitable than the protoxide,  $\text{Cu}_2\text{O}$ , because, on using the latter, part of the sulphide is converted into sulphate and hyposulphite. Johnson, No. 1352, 1862, again patented (for Burton) the desulphurization of  $\text{Na}_2\text{S}$  by  $\text{Cu}_2\text{O}$  (or  $\text{Fe}_2\text{O}_3$ ); even later Parnell obtained a patent (No. 2399, 1870) for employing zinc oxide, also Crockford (Nos. 1531 and 2024, 1871); and on April 3rd, 1876, Bazin and Wilden obtained a French patent simply for making caustic soda from sodium sulphide and cupric or ferric oxide.

M'Clintock (No. 2695, 1861) obtained provisional protection for the following process:—Seven parts sodium sulphate are fluxed with 8 parts copper oxide and 3 to  $3\frac{1}{2}$  parts coals; from the mass sodium carbonate is dissolved out, the remaining copper sulphide to be calcined to oxide, or regulus, or sulphate, &c.

Lalande (Germ. pat. 41991) employs the well-known reaction between  $\text{Na}_2\text{S}$  and zinc oxide, which is to be made more active by treating it with alkali, either hot or cold, but without being under the necessity of dissolving all the  $\text{ZnO}$ . So far as can be judged from Lequin's official Report on the Paris Exhibition of 1889, p. 97, the process offers no novelty; indeed when acting upon pure  $\text{Na}_2\text{S}$  with  $\text{ZnO}$  there must be at once a formation of  $\text{NaOH}$ , which is alleged to make the mass more active! Experiments made at the St. Gobain works showed a smooth reaction, but it was too difficult to filter the  $\text{ZnS}$  and recover the  $\text{ZnO}$  therefrom, much  $\text{ZnSO}_4$  being formed—just the same difficulties as have always occurred in former experiments in this direction.

*By sodium silicofluoride* (Claus, No. 3745, 1869).—Equivalent quantities of this compound and of sodium sulphide are heated by steam in a closed vessel. The reaction is:



The  $\text{H}_2\text{S}$  is collected and utilized in some manner. The residue, consisting of a solution of sodium fluoride and of silica, is, by treatment with calcium hydrate or carbonate, converted into  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  and  $\text{CaF}_2$ . The latter is mixed with the silica, treated with  $\text{HCl}$  and then with  $\text{NaCl}$ ; sodium silicofluoride is regenerated, as well as  $\text{HCl}$ , which can be obtained by distillation. Even the chlorine of the  $\text{NaCl}$  can be utilized if, instead of lime, magnesia be employed for decomposing the sodium fluoride. According to direct information from Mr. Claus, the reactions of this process are both quick and complete.

## CHAPTER XIV.

THE MANUFACTURE OF SODA FROM NITRATE OF SODA  
AND FELSPAR.

## FROM NITRATE OF SODA.

ALL the sodium nitrate which is required for the manufacture of nitric acid or directly used in vitriol-works is converted into acid sulphate (nitre-cake); and a large quantity of this is employed in alkali-making. There exists, however, a series of proposals for the direct utilization of nitrate in the alkali-manufacture.

*By means of coal*, by deflagration and lixiviation of the residue. —Duhamel (1735) was already aware of this reaction; Marggraf (1762) confirmed it; and Leuchs in 1844 still thought it applicable if nitrate was cheap enough! (Wagner's 'Regesten,' p. 55).

Fannie Brown (Engl. pat. 11008, 1884) mixes nitrate of soda with coal-dust, compresses the mixture and heats it to combustion. The mass is lixiviated, and the solution is brought to crystallization or converted into bicarbonate by means of the  $\text{CO}_2$  obtained by burning the carbon monoxide formed in the first reaction. [This "invention" is probably the outcome of popular evening classes on chemistry; Mrs. or Miss Brown has taken out no less than three patents in this connection.]

A. & G. Freda and Patroni (French pat. 206298) again patent the manufacture of alkaline carbonates from nitrates and charcoal, without any novelty.

*By manganese peroxide*.—Wöhler showed (1861) that on igniting sodium nitrate with  $\text{MnO}_2$  without access of air, the nitric acid is completely decomposed and a mixture of caustic soda with a lower oxide of manganese remains behind; not a trace of sodium manganate is formed (Ann. Chem. Pharm. cxix. p. 375).

*By potassium carbonate*.—Leuchs seems to have been the first to propose making potassium nitrate and sodium carbonate by mutually decomposing chemically equivalent quantities of sodium



nitrate and potassium carbonate. Anthon (1840) found this method to answer very well. Gentile (Dingl. Journ. cxviii. p. 200), Kuhlmann (Bull. Soc. d'Encourag. 1859, p. 567), Bolley (Dingl. Journ. clv. p. 418), Wöllner (Polyt. Notizbl. 1860, p. 49), Schnitzer (Dingl. Journ. clxii. p. 132), Schwarz (ib. clxiii. p. 314), and Grüneberg (ib. clxvi. p. 75) give explicit details on this process. Grüneberg seems to have been the first who, during the Crimean war (1854–55) and subsequently, manufactured potassium nitrate and sodium carbonate by this now abandoned process. Also the manufacture of potassium nitrate by means of caustic potash, with caustic soda as a by-product, belongs here (described by myself in Dingl. Journ. clxxxii. p. 388); but in all cases the potassium nitrate is the principal product, and soda only a by-product, while in the patent of De Sussex (No. 11263, 1846) it was proposed to decompose common salt by nitric acid and then convert the sodium nitrate into carbonate!

*By ammonium bicarbonate.*—The application of the ammonia-soda process for converting sodium nitrate into sodium bicarbonate and ammonium nitrate has been described, p. 155.

*By iron or other metals.*—Pollacci (Chem. News, xxvi. p. 288) heats a mixture of sodium nitrate with two or three times its weight of iron wire in an iron crucible or retort to a red heat; the mass is lixiviated with water: caustic soda is dissolved, and ferric oxide remains behind:



Wöhler (Ann. Chem. Pharm. lxxxvii. p. 373) employs cut-up copper foil for the same purpose. Neither of these processes has any practical interest. Heard (No. 7756, 1838) patented melting lead with sodium nitrate, treating the product with  $\text{CO}_2$  in closed vessels, and separating the soda from the white lead by lixiviation. Hill (Chem. News, xxvii. p. 170) points out that solutions of sodium nitrate at a high temperature are converted by zinc into caustic soda, ammonia, and hydrated zinc oxide; this could only become of technical importance, even with the present high price of ammonium salts, if the problem were solved of recovering the zinc from the hydroxide simply and cheaply.

In the Hargreaves process for converting pig-iron into malleable iron by means of nitrate of soda (which has never been worked on a large scale for any length of time), the soda passes into the slag

as carbonate, and the inventor proposed to recover it from the same (*Mechanics' Magazine*, 1868, p. 186).

*By magnesium or calcium sulphate.*—Kuhlmann (*Compt. Rend.* lv. p. 246) showed that sodium nitrate on being ignited with the above salts is converted into sulphate, whilst nitrogen tetroxide escapes, which on being brought into contact with air and water regenerates nitric acid. Thus sodium sulphate would be obtained along with nitric acid.

*By silica or alumina.*—Already in 1648 (Wagner's 'Regesten,' p. 56) Glauber knew that on igniting a mixture of saltpetre with clay, &c. nitric acid was expelled. Latterly attention has again been drawn to the fact of nitrate being decomposed by silica (Reich's saltpetre test, *Dingl. Journ.* clx. p. 357) and alumina (Wagner, in his 'Jahresbericht,' 1865, p. 250); thus sodium silicate or aluminate might be obtained, and by  $\text{CO}_2$  converted into soda, recovering  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Of course an indispensable condition is the complete recovery of the nitric acid from the nitrogen oxides. This process was patented in England (No. 2026, 1866) by Newton for Baker, Poole, and Stace; they wanted to employ the recovered nitric acid for decomposing common salt. Another patent by Baker is No. 2866, 1870.

According to experiments made by myself (*Dingl. Journ.* ccxliii. p. 157), vessels made of platinum, iron, or glass are strongly acted upon in the above reaction; even Berlin porcelain never stood more than one operation. The maximum decomposition (85 per cent.) was attained with the proportion 1 mol.  $\text{Al}_2\text{O}_3$  to 3 mols.  $\text{NaNO}_3$ . Had it been possible to stir the mass, probably less alumina would have been required, and the decomposition of the sodium nitrate might have been carried further. The recovery of the nitric acid, which in my laboratory experiment reached 89 per cent., might also have been improved. But the strong action on the material of the vessels deterred me from pursuing these experiments any further.

*By calcium carbonate.*—Walz (Wagner's *Jahresb.* 1869, p. 182) heats sodium nitrate with calcium carbonate and steam in retorts, condenses the nitric acid, of which almost the theoretical quantity is obtained, and utilizes the residue, consisting of sodium carbonate and lime, either directly or after lixiviating with cold water, for making caustic soda. Exactly the same thing was patented in Prussia by Lieber in 1867 (*Deutsch. chem. Ges. Ber.* viii. p. 49);

after nine months' working he was obliged to give up the process, owing to the strong corrosion of all the vessels.

I myself had experiments made in my laboratory (Dingl. Journ. ccxxxviii. p. 69), in which the decomposition was carried out in strong platinum boats, heated in a porcelain tube by a coal-fire as high as possible. When employing 150 parts of  $\text{CaCO}_3$  to 100  $\text{NaNO}_3$ , the latter was completely transformed into  $\text{NaOH}$  and most of the nitric acid was recovered. In an open boat this decomposition could be achieved on a Bunsen burner. But even platinum vessels were destroyed in a short time, so that the process could not be carried out in practice.

F. M. Lyte (Engl. pat. 5352, 1891) employs this process in order to utilize the nitric acid for making lead nitrate, which is transformed by  $\text{NaCl}$  into lead chloride and sodium nitrate. The lead chloride is thus electrolyzed, and the sodium nitrate is employed as before (comp. Chapter XXVII.).

Vogt (Engl. pat. 22018, 1891) heats sodium nitrate with quicklime in a current of previously heated  $\text{CO}_2$  gas at  $350^\circ \text{C}$ .; sodium carbonate is formed and nitrous fumes escape which are oxidized into nitric acid. The presence of steam and heated air is useful in this oxidation. The  $\text{CO}_2$  is also from the outset mixed with steam. By introducing the  $\text{CO}_2$  from without, the temperature can be regulated at will, and the direct heating of the apparatus need not be carried to the same degree. The mass must, at all events, be porous, so that the  $\text{CO}_2$  may penetrate and the nitrous vapours may escape; hence the necessity of admixtures, for which (besides quicklime) magnesia, baryta, strontia, the carbonates of the alkaline earths, and the oxides of manganese or iron may be employed. The temperature of decomposition need not exceed  $350^\circ \text{C}$ . from the beginning to the end.

Garroway (Engl. pat. 7412, 1894) heats a mixture of sodium nitrate with  $1\frac{1}{2}$  times its weight of quicklime (or baryta, strontia, or magnesia) in a current of superheated steam and, if necessary, also with some heated air in cast-iron retorts; the nitric acid is condensed, and the residue is worked for caustic soda. The retorts are heated by the waste heat of pyrites burners or in any other way.

*With ferric oxide.*—In 1862 Mond took out provisional protection (No. 2556) for preparing nitric acid from sodium nitrate by heating the latter with basic or indifferent substances, not

fusing at a high temperature or otherwise changing, like the oxides of iron, manganese, copper, cobalt, or nickel. The vapours were to be passed into vitriol-chambers, or nitric acid was to be recovered from them by cold water. The residue may be advantageously worked for caustic soda. [This last must have appeared to him as a secondary detail, since it is not mentioned in the title, and therefore it could not have been included in the claims, even if the patent had been completed, which was not the case. Nothing is said of the formation of a chemical compound in the case of ferric oxide being employed; in the case of the other oxides no such compound could have been thought of at all.]

Bradburn (Engl. pat., by Thompson, No. 6710, 1889) mixes 2 mols. NaCl with 4 mols. nitric acid and 1 mol.  $\text{MnO}_2$  (or a manganate or permanganate), and heats the mixture in an earthenware retort, whereupon the following reaction takes place (comp. Schloesing's chlorine process, Chap. XXIII.) :



The chlorine is employed in the usual manner. From the residue the manganese is precipitated by caustic soda, and  $\text{MnO}_2$  is recovered by means of air, in order to be used over again in the first stage. The sodium nitrate remaining in solution is recovered by evaporation, mixed with ferric oxide and heated in a current of air. The mixture of nitrous gases is conveyed over an oxidizing compound of manganese and nitric acid recovered therefrom. The residue in the furnace on lixiviation furnishes a solution of caustic soda and ferric oxide, which can be used over again.

F. M. Lyte (Engl. pat. 8692, 1891) decomposes sodium nitrate with ferric oxide, and otherwise proceeds as in his patent No. 5352, 1891; comp. p. 257.

This process, which had never been experimentally tried, was worked out in detail by myself, and forms the subject of patents by Lunge and Lyte (Nos. 13654 and 13655, 1893). It is absolutely necessary to keep the mixture of sodium nitrate and ferric oxide in a porous state, in order to make it permeable for the gases, when being treated with heated air and steam, as is there described. The sodium nitrate must therefore be intimately mixed with about twice its weight of iron oxide in as pure a state as possible, *e. g.* "purple ore," which can be done very well by evaporating the solution after adding the ferric oxide. It

depends upon the nature of the ferric oxide, that is its physical state, how much has to be employed to obtain a porous mass not fusing during the process. The mixture is put into a retort, and a current of heated air and superheated steam is forced through it; the retort is also heated from without. The decomposition is most perfect, and takes place at a lower temperature, if neither steam nor air is used alone, but a mixture of both is employed. The quantity of steam is regulated in such manner that the nitric acid recovered from the escaping fumes does not turn out too weak, and the quantity of air is kept in sufficient excess to transform the lower nitrogen oxides into nitric acid by means of a Lunge-Rohrmann plate-tower or other suitable apparatus. (About 95 per cent. of the total nitric acid can be thus recovered.)

The residue in the retort is a greenish mass, consisting of a chemical compound of soda and ferric oxide (sodium ferrite), mixed with an excess of ferric oxide. By heating with water it is decomposed, and a concentrated, perfectly pure, solution of caustic soda is obtained; the ferric oxide originally combined with the soda is separated in such finely divided form that it can be extracted from the excess of crude iron ore and employed as Venetian red or the like.

The same process is also employed in the manufacture of white lead according to the patent of Lunge and C. H. Maxwell Lyte (No. 13656, 1893), and caustic soda is thus obtained as a by-product.

The connection of these processes with the manufacture of chlorine by the electrolysis of lead chloride will be described in Chapter XXVII.

#### FROM SODA-FELSPAR.

This has been attempted several times. For instance, as No. 2983, 1856, Newton patented (as a communication) the heating of felspar with lime and calcium phosphate, whereby caustic alkalies were to be formed.

The only proposals in this direction offering any prospect of success are those made by Ward and Wynants (patents No. 3185, 1857, and No. 1375, 1864; comp. also Hofmann's 'Report by the Juries,' p. 51). Felspar, ground as finely as Portland cement, is mixed with a quantity of flour-spar equivalent to the alkali

contained in it, or with cryolite, also with chalk and calcium hydrate; and the whole is exposed to the heat of a cement-kiln. The mass frits, but, owing to the lime, remains porous and easy to lixiviate with water: the alkali of the felspar (potash or soda) dissolves as caustic; and the residue may be utilized as cement. Hofmann (*l. c.*) reports the splendid success of this process in recovering the *whole* of the potash contained in the felspar; Dullo (Wagner's *Jahresb.* 1865, p. 291) contests both the possibility of this and of employing the residue as a cement. In any case the cost of the process of Ward and Wynants renders it quite inapplicable to soda-felspar, even if it could be applied to potash-felspar, which is not to be thought of at present.

### THIRD BOOK.

## THE CHLORINE INDUSTRY.

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### CHAPTER XV.

#### GENERAL.

THE bleaching- and the soda-industry are intimately connected; for by far the largest portion of the hydrochloric acid arising as a by-product in alkali-making is worked up for bleaching-compounds. The present low price of soda-ash is only possible by the profit made in manufacturing bleaching-powder. It is a remarkable coincidence that the discovery of chlorine and of chloride of lime happened about the same time as the invention of artificial soda and the working-out of Leblanc's process, so that from the first both industries could work together. The gas given off by aqua regia, which contains chlorine, was already known to Van Helmont; Glauber also (1648) and Boyle (1661) seem to have had it under their hands; but the undisputed discoverer, properly so called, of chlorine itself was Scheele, who described it in his treatise on manganese, in 1774, mentioning at the same time its bleaching action on vegetable colours. He did not take it for an element, but for "dephlogisticated muriatic acid." The hydrate of chlorine was discovered in 1785 by Pelletier, and in 1786 by Karsten, both of whom took it for solid chlorine, till Davy showed, in 1810, that it contains water. Faraday, in 1823, analyzed it quantitatively, and on that occasion obtained chlorine condensed to a liquid.

The industrial employment of the bleaching-properties of chlorine, discovered by Scheele, was first suggested by Berthollet in 1785. He at first used chlorine-water; but from 1789 the chlorine was passed into potash liquor at the Javel works near Paris, whence chloride of potash is still called "eau de Javel." Here

the celebrated James Watt saw the new bleaching-process, and in 1786 introduced it into the works of his relative MacGregor at Glasgow. It would appear that already in July 1787 Milnes and Gordon, Barrow, and Co., at Aberdeen, had employed chlorine for bleaching on a large scale, in consequence of the observations made by Professor Copeland and the Duke of Gordon in France (Mactear, Report &c. p. 16; Kingzett, 'Alkali Trade,' p. 180). According to Keyworth (Chem. News, xxxiii. p. 131), Robert Hall, of Basford Hall, near Nottingham, was the first to apply chlorine on a manufacturing-scale to the bleaching of fabrics; but as no date is given, this statement is of little account. On March 25th, 1789 (No. 1678), de Boneuil patented for England the manufacture of chlorine-water and its application for bleaching; the same was again done by C. and G. Taylor (No. 1872, 1792), by Campbell (No. 1922, 1792), by Bigg (No. 2040, 1795; application to paper-stuff), by Lord Dundonald on the same day (No. 2043), and by Carpenter on Nov. 19, 1795. But the most important step was taken by Charles Tennant, in his patent of Jan. 23rd, 1798 (No. 2209). In this he describes the employment of lime, strontia, or baryta, instead of alkalies, for "neutralizing the oxy-muriatic acid," but only suspended in water; so that he obtained the compound at present known as "bleach-liquor." Tennant at that time carried on a bleach-works at Darnley; and he soon commenced manufacturing bleach-liquor in partnership with MacIntosh. This was already a vast improvement, since the then enormously dear alkalies were replaced by milk of lime; but the still greater advance, the employment of dry calcium hydrate instead of milk of lime, and consequently the preparation of a more stable and more portable form of bleaching-compound, was made in the following year, after Tennant's patent had been invalidated owing to anticipation (probably by Lancashire bleachers). He now took out a fresh patent (on April 30, 1799, No. 2312), for absorbing chlorine by *dry* hydrate of lime (baryta, or strontia), and in the same year started the St.-Rollox works near Glasgow, which for many years have been the largest bleaching-powder works. From the tables given by Mactear (*op. cit.* p. 18) it appears that 52 tons, at a price of £140 per ton, were manufactured in 1799–1800; in 1805 only 147 tons at £112; in 1820, 333 tons at £60; in 1825 (muriatic acid being already employed), 910 tons at £27; in 1870, 9251 tons at £8 10s.



*Properties of Chlorine.*

We have already seen that chlorine was discovered by Scheele in 1774. He called it dephlogisticated muriatic acid, to which name Berthollet's designation of oxymuriatic acid corresponds. The radical of muriatic acid was itself believed to be a compound body, being supposed to contain oxygen. Many chemists adopted this view; but it was shaken when Gay-Lussac and Thénard in 1806 could not isolate any oxygen from chlorine. Still Berthollet's view of the compound nature of chlorine was adhered to, till Davy in 1810 adduced new arguments for its elementary nature, and gave it the name "chlorine" (from *χλωρός*, green). Davy himself pointed out that his view was not essentially different from that of Scheele. Most chemists adopted Davy's explanation at once; but some opposed it, especially Murray (1811) and Berzelius (1812-15); and it was only in 1821 that the latter, and the rest with him, finally came over to Davy's view.

The colour-destroying compounds which chlorine forms with aqueous solutions of the alkalis were first recognized by Berthollet; they were especially examined by Balard (1831), who also discovered free hypochlorous acid. Berthollet also prepared some chlorates; Gay-Lussac, in 1814, free chloric acid.

Chlorine is a greenish-yellow gas, and is darker in proportion as it is hotter. Its specific gravity, calculated from Stas's atomic weight, is 2.45012; it was observed by Bunsen to be = 2.4482. Landolt and Börnstein state it, calculated for sea-level in the latitude of Berlin, = 2.4492.

In the anhydrous state chlorine has not yet been solidified under ordinary pressure at  $-40^{\circ}\text{C.}$ ; but under a pressure of 4 atmospheres already at  $+15^{\circ}\text{C.}$  it forms a clear yellow liquid of spec. grav. 1.33, which does not freeze at  $-90^{\circ}\text{C.}$ , and boils at  $-33^{\circ}.6$  under a pressure of 760 millims. Chlorine gas is not combustible, but supports the combustion of many organic compounds with a strongly fuliginous flame. It does not act upon dry litmus-paper when perfectly dry itself, but in the moist state destroys its colour, as well as most other vegetable dyes. It also destroys organic smells and infectious matters, and is consequently of great value as a disinfectant. Its smell is extremely suffocating; it causes, when inhaled in very slight quantity, cold in the head, general irritation of the epithelium, coughs, suffocating sensations, vomiting, and, if more frequently breathed, spitting of blood. As an

antidote, the inhalation of sulphuretted hydrogen, alcohol or ether vapour, or aniline vapour is recommended; the workmen employ rum as an internal remedy. According to Lehmann, an admixture of 2 to 4 millionths chlorine with air is borne without injury; those accustomed to it may tolerate 1 vol. in 10,000 of air. Weigelt (Chem. Zg. 1880, p. 39) found that 0.005 grm. free chlorine per litre would kill trout in a few minutes, 0.002 grm. after a longer interval.

Chlorine occurs uni-, tri-, quinq-, and septivalent, viz. univalent in all chlorides and organic compounds, tri- to septivalent in its oxides. Its atomic weight has been frequently determined—most accurately by Stas, whose result (oxygen=16) is 35.457 or (hydrogen=1, oxygen=15.96) =35.368. For calculations 35.5 is usually assumed. A litre of it at 0° C. and 760 millims. weighs 3.1691 grams. Its chemical affinities in most cases are much more energetic than those of oxygen. Equal volumes of chlorine and hydrogen mixed together are caused to combine not only by the electric spark or a red-hot body, but even by the sunlight, with a violent explosion.

At a little above 0° C. chlorine combines with water and forms a solid mass. From saturated chlorine-water in the cold there crystallizes *chlorine hydrate*,  $\text{Cl} + 5\text{H}_2\text{O}$ , or  $\text{Cl}_2 + 10\text{H}_2\text{O}$ , with 28.29 per cent. chlorine. Göpner (Deutsch. chem. Ges. Ber. viii. p. 287) assigns to it the formula  $\text{HOCl}, \text{HCl}, 9\text{H}_2\text{O}$ , i. e. a common hydrate of hydrochlorous acid and hydrochloric acid. Schiff (*ib.* p. 419), to whom Göpner referred, declines this view, since such a concentrated solution of hypochlorous acid is quickly decomposed at 20° C., and it is not conceivable that the presence of a molecule of HCl should convert it at 10° C. into such a stable compound as chlorine hydrate. This forms an arborescent, crystalline, pale yellow, transparent mass of specific gravity about 1.2; Faraday observed it in needles and rhombic octahedra, Biewend in tesseral crystals. At -50° C. it is almost white. At the ordinary temperature and pressure it dissociates into chlorine gas and chlorine-water; in sealed tubes it remains unchanged even in the heat of summer; but at +38° it splits up into chlorine-water and liquid chlorine. (The dissociation of chlorine hydrate has been fully investigated by Isambert, Compt. Rend. lxxxvi. p. 481.) This hydrate is frequently formed in winter in the pipes conveying the gas in bleaching-powder works when exposed to the cold, and sometimes stops up the pipes completely.

Water absorbs chlorine gas most amply at 10° C.; from 9° to 40° its solubility decreases, because it is then in the state of hydrate. At 0° C. one part of water dissolves 1·43 (Gay-Lussac) or 1·80 (Pelouze) part of chlorine. At 100° its solubility is=0. Saturated chlorine-water at 6° has the specific gravity 1·003; it is greenish yellow, smells of chlorine, and has an astringent but not acid taste. It freezes at 0°, and splits up into chlorine hydrate and ice free from chlorine.

According to Schönfeld (Ann. Chem. Pharm. xciii. p. 26, cxv. p. 8), the coefficient of absorption of chlorine gas from 11° to 41°·5 C. is =3·0361—0·046196*t*+0·0001107 *t*<sup>2</sup>. According to him 1 vol. of water absorbs the following volumes of chlorine (calculated at 0° C. and 760 millims.) :—

At	Vols. of chlorine.	At	Vols. of chlorine.	At	Vols. of chlorine.
10°C...	2·5852	21°C...	2·1148	31°C...	1·7104
11.....	2·5431	22.....	2·0734	32.....	1·6712
12.....	2·4977	23.....	2·0322	33.....	1·6322
13.....	2·4543	24.....	1·9912	34.....	1·5934
14.....	2·4111	25.....	1·9504	35.....	1·5550
15.....	2·3681	26.....	1·9099	36.....	1·5166
16.....	2·3253	27.....	1·8695	37.....	1·4785
17.....	2·2828	28.....	1·8295	38.....	1·4406
18.....	2·2405	29.....	1·7895	39.....	1·4029
19.....	2·1984	30.....	1·7499	40.....	1·3655
20.....	2·1565				

Solutions of chlorides, as NaCl &c., absorb less chlorine than pure water. Chlorine mixed with H or CO<sub>2</sub> is absorbed by water more largely between 13° and 38° than corresponds to its partial pressure (Roscoe). Chlorine-water decomposes gradually, especially in the light, into hydrochloric acid and oxygen gas.

Pedler experimented in Calcutta (Journ. Soc. Chem. Ind. 1890, p. 65) on the influence of tropical sunlight on the action of chlorine upon water, in sealed tubes. If 1 mol. chlorine (Cl<sub>2</sub>) was present to 64 mols. H<sub>2</sub>O, no action took place even after a month's insolation; with 1:88 the reaction was quite pronounced, with 1:150 about 50 per cent. of the chlorine was exchanged for oxygen, with 1 Cl<sub>2</sub> to 400 H<sub>2</sub>O 80 per cent. Saturated chlorine-water (containing in Calcutta 1 mol. Cl<sub>2</sub> to 708 mols. H<sub>2</sub>O) is almost completely decomposed by sunlight according to the

equation:  $2\text{H}_2\text{O} + 2\text{Cl}_2 = \text{O}_2 + 4\text{HCl}$ ; here chloric acid is formed to a very slight extent. In diffused daylight, however, along with oxygen hypochlorous and chloric acid are largely formed.

Since liquefied pure chlorine has become a commercial article, the properties of liquid chlorine have acquired greater interest. According to Knietzsch (Lieb. Ann. cclix. p. 100) liquid chlorine in thick layers is yellow with an orange tint. He examined the vapour-tensions from  $-102^\circ$  up to the critical point ( $+146^\circ$ ), as well as the specific gravities and coefficients of expansion at various temperatures, which he indicates in the following table:—

Temperature.	Pressure.	Spec. gravity.	Average coefficient of expansion.
$-102^\circ$	solid.	—	
$-88$	37.5 mill. Hg.	—	
$-85$	45.0	—	
$-80$	62.5 "	1.6602	0.001409
$-75$	88.0 "	1.6490	
$-70$	118 "	1.6382	
$-65$	159 "	1.6273	
$-60$	210 "	1.6167	
$-55$	275 "	1.6055	
$-50$	350 "	1.5945	
$-45$	445 "	1.5830	
$-40$	560 "	1.5720	
$-35$	705 "	1.5589	
$-33.6$	760 "	1.5575	0.001793
$-30$	1.20 atm.	1.5485	
$-25$	1.50 "	1.5358	
$-20$	1.84 "	1.5230	
$-15$	2.23 "	1.5100	
$-10$	2.63 "	1.4965	
$-5$	3.14 "	1.4830	
$0^\circ$	3.66 "	1.4690	
$+5$	4.25 "	1.4548	
10	4.95 "	1.4405	0.001978
15	5.75 "	1.4273	0.002030
20	6.62 "	1.4118	
25	7.63 "	1.3984	0.002190
30	8.75 "	1.3815	
35	9.95 "	1.3683	0.002260
40	11.50 "	1.3510	
50	14.70 "	1.3170	0.002390
60	18.60 "	1.2830	
70	23.00 "	1.2430	0.003460
80	28.40 "	1.2000	
90	34.5 "		
100	41.7 "		
110	50.8 "		
120	60.4 "		
130	71.6 "		
146	93.5 "		

## CHAPTER XVI.

THE MANUFACTURE OF CHLORINE BY MEANS OF  
MANGANESE ORE.

CHLORINE is very widely diffused in nature, mostly in combination with sodium; most of it is up to this day made from sodium chloride. Potassium chloride is technically equivalent to this, inasmuch as large quantities of KCl are transformed into potassium sulphate for the sake of manufacturing potassium carbonates (artificial potashes), in which case the hydrogen chloride set free in the operation is treated exactly as in the case of common salt, and, if not sold as such, can be converted into chlorine. Other sources of chlorine are the chlorides of the alkaline earths, among which, above all others, magnesium chloride is important, not merely because it occurs in very large quantities as a by-product in the manufacture of potassium chloride, but also because free chlorine is much more easily split off from it than from the alkaline chlorides. This has produced great expectations for many years past, and has called forth very numerous experiments, but hitherto without any considerable success, as we shall see later on.

Practically, apart from electrolysis (which will be treated in a separate section of this volume), chlorine is almost exclusively manufactured by means of *hydrochloric acid*, either by treating this immediately in the form of a gas, as it is formed in the reaction of sulphuric acid on sodium chloride (Deacon's process, &c.), or first condensing it by water and then treating the liquid hydrochloric (muriatic) acid. In all cases the hydrogen of the HCl must be removed by an oxidizing agent. Formerly, apart from mere experiments with other oxidizing substances, the agent exclusively employed for this purpose was *manganese dioxide*, either in the shape of native manganese ore or in that of "recovered manganese" (Weldon mud). Then came the oxidation by

atmospheric oxygen with the assistance of catalytic substances (Deacon's process), which was succeeded by other processes working with atmospheric oxygen. Of other oxidizing agents we will in this place only mention nitric acid.

In this Chapter we describe the formerly exclusively employed method of manufacturing chlorine from manganese ore and hydrochloric acid, which up to this day is used wherever comparatively small quantities of chlorine must be prepared for direct consumption. For the storing of chlorine in a solid form for subsequent use, as bleaching-powder or chlorates, this old process can no longer compete; but in the Weldon process the loss of manganese must be still made up by employing some manganese ore in the old way.

#### THE MANGANESE ORES.

Technical "manganese ore" or "manganese" is mostly a mixture of the following minerals:—

*Pyrolusite*,  $\text{MnO}_2$ , containing 18.2 per cent. active oxygen.

*Polianite* is also  $\text{MnO}_2$ , but much harder and crystallizing in a different way.

*Braunite*,  $\text{Mn}_2\text{O}_3$ , with 10 per cent. active oxygen, usually considered to be a salt of the formula  $\text{MnO}, \text{MnO}_2$ .

*Brown manganese ore*, *manganite*,  $\text{Mn}_2\text{O}_3, \text{H}_2\text{O}$ .

*Varvicite* and *newkirkite* are varieties of manganite.

*Hausmannite*,  $\text{Mn}_3\text{O}_4 = 2\text{MnO}, \text{MnO}_2$ , with only 6.95 per cent. active oxygen.

*Psilomelan*, of complicated composition.

*Wad* is a product of the decomposition of other manganese ores.

A mineralogical description and many analyses of these ores are found in our first edition, Vol. III. pp. 114 to 119; these are not repeated here, as natural manganese ore has lost much of its importance for the chlorine industry since that time. More modern analyses of Russian ores are found in Dingl. Journ. ccxlviii. p. 471; of Transcaucasian ores in Journ. Soc. Chem. Ind. 1889, p. 226; of Chilian ores (by J. and H. S. Pattinson) in the same journal 1889, p. 676; of the European ores (by Gorgeu) in Bull. Soc. Chim. 1890, [3] iii. p. 248, and 1893, [3] ix. p. 497.

Most of the manganese ores do not now serve for the manufacture of chlorine, but for that of iron and steel, for which purpose

their value does not depend upon their percentage of active oxygen, but upon that of manganese metal.

The more important occurrences of manganese ore were up to the middle of this century the German ones, at Ilmenau and Elgersburg in Thuringia, Ihlefeld in the Harz, Giessen, Nassau, Siegen. This ore, as it reached the chemical works, only averaged 60 per cent.  $\text{MnO}_2$ ; since 1860 it was more and more put into the background by the richer Spanish ore, from the district of Huelva. A little manganese ore is also mined in Devonshire and at Romanèche in France. In 1868, about the time when the Weldon process was introduced, the consumption of manganese ore for the chlorine manufacture in England amounted to 54,000 tons. In consequence of the introduction of the Weldon and Deacon processes the consumption for chlorine-making decreased enormously, and in 1888 it amounted to only 7000 tons (Pattinson, Journ. Soc. Chem. Ind. 1889, p. 677). Since 1880 a large quantity of manganese ore has found its way into commerce, intended and fit only for the iron manufacture; the statistical figures do not distinguish between this ore and that which serves for the chlorine manufacture. New localities have been discovered from which very large quantities of manganese ore are exported, principally Caucasia and Chile, also New Zealand, Greece, North America, Canada, Australia. A bed has recently been discovered at Gosalpur, in India.

In Chile the principal mines (described in Chem. Zeit. 1887, p. 1620) are found in the provinces of Atacama and Coquimbo. In Russia the principal mines in the Caucasus are near the village of Chiatur, district of Sharopan, province of Kutais (detailed description in Zsch. f. angew. Ch. 1890, p. 302). In Transcaucasia the mining commenced in 1879 with an output of 871 tons, and in 1890 it had already risen to 182,468 tons, by far the largest in the world.

The *statistics* of manganese ore have no great value for the chlorine industry, as they do not distinguish between that which serves for the manufacture of iron and that which is fit for chlorine, as just mentioned. Thus, *e.g.*, the United States, where hardly any chlorine products are manufactured, in 1893 consumed more than 60,000 tons of manganese ore, 6000 tons of which was mined in the country, the remainder being imported from Russia, Chile, and Cuba. The output in the different countries varies enormously,

regarding which I must refer the reader to Rothwell's 'Mineral Industry,' vol. ii. p. 470 (New York, 1894). Here I will only quote the figures relating to the production of all kinds of manganese ore in 1892:—

	Metrical tons.		Metrical tons.
Austria .....	4558	Hungary .....	1304
Belgium .....	16775	Italy .....	1243
Bosnia .....	7944	Japan (1891) ...	3249
Canada .....	105	New Zealand ...	529
Chile .....	50000	Portugal .....	3399
Cuba .....	18000	Russia .....	113081
France .....	15000	Australia .....	861
Germany .....	32891	Spain .....	9002
England .....	6175	Sweden .....	7832
Greece .....	11716	United States ...	19425

The British production (chiefly in Devonshire) was:—

Year.	Tons.	Year.	Tons.
1888 .....	4342	1891 .....	9632
1889 .....	8852	1892 .....	6175
1890 .....	12444		

The German production was:—

Year.	Tons.	Year.	Tons.
1888 .....	28710	1891 .....	40325
1889 .....	45167	1892 .....	32891
1890 .....	41841		

Chemists are now agreed in attributing to manganese dioxide the quality of an acid; they regard hausmannite as  $2\text{MnO}, \text{MnO}_2$ , and braunite as  $\text{MnO}, \text{MnO}_2$ . Christensen (Journ. Soc. Chem. Ind. 1883, p. 346) endeavoured to show that the constitution of braunite is the same as that of hematite,  $\text{Fe}_2\text{O}_3$ . Spring and Lucion (Bull. Soc. Chim. 1890 [3] iii. p. 4), however, return to the formula  $\text{MnO}, \text{Mn}_2$ ; but that of the dioxide they do not write  $\text{MnO}_2$ , but  $\text{Mn}_2\text{O}_4$ , or even  $5(\text{MnO}_2) = 3\text{MnO}, \text{Mn}_2\text{O}_7$ .

A large number of important papers on the oxides of manganese have been published by Gorgen since 1879. Here we shall only briefly refer to the most recent of these. He prepared *artificial manganese dioxide* (Bull. Soc. Chim. 1888, xlix. p. 757) by heating natural manganite, from Ihlefeld,  $\text{Mn}_2\text{O}_3, \text{N}_2\text{O}$ , during six hours



between  $275^{\circ}$  and  $310^{\circ}$ . The active oxygen rose from 10.10 to 18.10 per cent. (theory for  $\text{MnO}_2$ : 18.40). The heating must take place at a temperature at which the water of hydration is only slowly expelled. He did not meet with the same result in the case of the other native ores, nor in that of artificial manganese carbonate. He considers polianite to be a direct natural product, but pyrolusite to be a product of the modification of other ores. He further describes the preparation of  $\text{MnO}_2$  in the wet way by various methods (Bull. Soc. Chim. 1890, [3] iv. p. 16). He shows that this oxide ("manganous acid") exists both as an anhydride, in the state of polianite and pyrolusite, and in that of a hydrate, and that it exhibits indubitably acid properties, not merely towards free bases, but also in displacing carbonic acid, acetic acid, and even sulphuric acid from their salts.

Another recent paper on the basicity of  $\text{MnO}_2$  is that by Rousseau (Compt. Rend. cxvi. p. 1060). Its normal salts are bivalent, *e. g.*  $\text{BaO}$ ,  $\text{MnO}_2$ ; but under certain conditions  $\text{MnO}_2$  acquires greater saturating capacity, so that it is possible to produce a compound  $2\text{CaO}$ ,  $\text{MnO}_2$ .

*The commercial value of manganese ore for producing chlorine* of course depends first of all upon the oxygen present over and above that necessary to form  $\text{MnO}$ , because it is this only that evolves chlorine from hydrochloric acid. As a rule this is not expressed in parts per cent. of oxygen, but of manganese dioxide; *e. g.* pure manganese sesquioxide is calculated as if it were  $\text{MnO} + \text{MnO}_2$ , red manganese oxide as  $2\text{MnO} + \text{MnO}_2$ , &c. When it is stated that an ore contains 60 or 70 per cent.  $\text{MnO}_2$ , this only means that 100 parts of it liberate as much chlorine as 60 or 70 per cent. pure  $\text{MnO}_2$  would do. But the presence of  $\text{MnO}$  is not indifferent, since it consumes acid as well, and too large a percentage of it may make an ore, otherwise pure, worthless on account of consuming too much hydrochloric acid. Of the remaining constituents of ordinary manganese ores, some are comparatively harmless, but others, such as ferric oxide, are injurious because they consume  $\text{HCl}$ , and  $\text{FeO}$  because it absorbs oxygen. Even the insoluble matters, like barium sulphate and silica, are frequently very injurious, because they mechanically obstruct the action of  $\text{HCl}$ ; often in the chlorine-stills lumps of substances are found covered with silica, but consisting inside of unchanged manganese ore. More injurious than anything else are the car-

bonates of calcium &c., as they not only consume acid but give off  $\text{CO}_2$ , which exerts an extremely harmful influence in the manufacture of bleaching-powder. In England ores containing upwards of 1 per cent.  $\text{CO}_2$  are not considered marketable. Such ores can be almost completely deprived of the carbonates by crushing and treating with dilute acids or acid still-liquor; but this is always an expensive process.

The physical state of manganese ore is also of importance for its value. Generally the soft descriptions are much superior to the hard ones, because they are more easily dissolved in the acid and require a smaller excess of it than the latter; there exist some ores of high strength but such hardness that they can only be dissolved by a great excess of acid and steam, and consequently have only a small value. All these things must be considered when buying manganese.

The *consumption of hydrochloric acid* is not usually estimated directly, but is felt in the following custom of the trade. The normal percentage for German manganese is 60 per cent.  $\text{MnO}_2$  in the dry state; each 1 per cent. above or below that strength is paid for at a certain rate, usually 2s. per ton; nothing below 57 per cent.  $\text{MnO}_2$  is accepted. For Spanish and similar ores the normal strength is 70 per cent., with a bonus of 2s. 6d. per cent. up or down, 65 per cent. being the minimum allowed. The price of 70-per-cent. manganese is much higher than if it were calculated on the basis of 60 per cent. The minimum of carbonic acid allowable is usually stated at 1 per cent., sometimes at  $\frac{1}{2}$  per cent.

#### *The Valuation of Manganese Ore.*

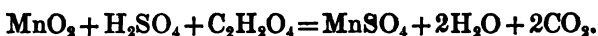
Manganese ores are always tested for moisture, for active oxygen (expressed as  $\text{MnO}_2$ ), and for carbonic acid. Sometimes also the quantity of hydrochloric acid required for decomposing it is estimated.

1. *Moisture*.—There is no perfect agreement in this case. Fresenius pointed out that manganese loses its hygroscopic moisture at  $100^\circ \text{C}$ . very slowly and not quite completely, but at  $120^\circ \text{C}$ . completely; if that temperature is exceeded, the chemically combined water also begins to be expelled. Fresenius constructed a peculiar drying-apparatus for manganese, consisting of a thick cast-iron dish with a number of holes in which small numbered

brass pans, containing the samples, are placed. In England the drying is always done at 100° C., which is against the seller, since the higher percentage of completely dry manganese ore makes it much more valuable than in the simple ratio of the moisture lost. But then the extremely finely ground sample ought to be kept in a very thin layer at 100° C. for at least six hours, and it must be weighed after cooling in a desiccator.

2. *Active Oxygen (Manganese Dioxide).*—The results of testing for active oxygen—that is, that which is in excess of MnO and which therefore yields chlorine with HCl—are always expressed in percent. MnO<sub>2</sub>. 1 part of active oxygen = 5.438 parts MnO<sub>2</sub>. There are a great many methods for estimating this.

One of the oldest is that of Gay-Lussac:—boiling the ore with concentrated sulphuric acid, by which the active oxygen is evolved in the free state; it is measured as such after the CO<sub>2</sub> has been absorbed. This plan is hardly ever tried now. The most widely used method was formerly the oxalic-acid method, originally proposed by Berthier and Thompson, but first worked out in a proper form by Fresenius and Will. The reaction is:

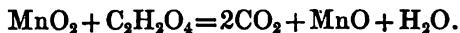


If the ore is gently heated with sulphuric and oxalic acid and the evolved gas is deprived of its moisture before escaping, the loss of weight is a measure of the active oxygen, since 2 mols. CO<sub>2</sub> always correspond to 1 atom of O or 1 mol. MnO<sub>2</sub>. Of course the CO<sub>2</sub> already present should be estimated by a special experiment, or it must be allowed to escape by treating the sample with sulphuric acid before adding the oxalic acid and weighing the apparatus.

This method can be carried out in different ways. It was mostly performed in one of the well-known apparatus for estimating the loss of weight, by weighing before and after the reaction: this apparatus must always possess an arrangement for drying the gas by means of sulphuric acid or calcium chloride. It is hardly possible to perform this operation quite accurately, as the apparatus is rather heavy, and the condensation of moisture on the complicated glass surface is not the same before and after the heating, even when keeping it both times in the balance-case. It also easily happens that the gas is not completely dried before escaping. The results, for this reason to begin with, are not at

all uniform, especially in the hands of different operators, and the method referred to has long ceased to be considered the normal one. It becomes rather more accurate if the  $\text{CO}_2$  is not estimated by loss of weight, but by absorption in soda-lime or the like; but there are sources of error in this case also. One of these is that the harder descriptions of manganese, in spite of the finest grinding, can only be dissolved with the help of prolonged heating, almost inevitably causing some  $\text{CO}_2$  to escape unabsorbed. It has also been reproached with not entirely oxidizing the magnetic iron oxide ( $\text{Fe}_3\text{O}_4$ ) which frequently occurs in manganese ores; this, however, is completely oxidized to  $\text{Fe}_2\text{O}_3$  when the ore is employed for the production of chlorine. For this reason, in 1869 the English union of alkali-manufacturers altogether rejected the Fresenius-Will process. Pattinson (*Chem. News*, xxi. p. 267) proved that reproach to be unfounded, as the lower oxides of iron in this process are always oxidized up to  $\text{Fe}_2\text{O}_3$ ; but still he prefers the iron method, on account of its greater certainty in operation, especially with hard ores. In order to lessen the errors in the Fresenius-Will process, all cork joints should be covered with wax or paraffin, and the apparatus be allowed to cool *completely* and remain some time in the glass case of the balance before weighing.

Another way of employing the same reaction is to treat the ore with a known quantity of oxalic acid and retitrate the unused portion of the latter. About 2 grams of very finely ground manganese are heated with 50 cubic centims. of normal oxalic-acid solution and 5 or 6 cubic centims. of strong sulphuric acid, till the completeness of the decomposition is indicated by the black colour of the sediment vanishing entirely; then, without filtration, after dilution with water, the liquid is retitrated with standard permanganate solution at  $60^\circ\text{C}$ ., till a pink colour appears: or only an aliquot portion of the liquid may be treated in this way. Each 90 parts of oxalic acid (calculated as anhydrous) thus indicated as destroyed correspond to 86 parts of  $\text{MnO}_2$ ; for

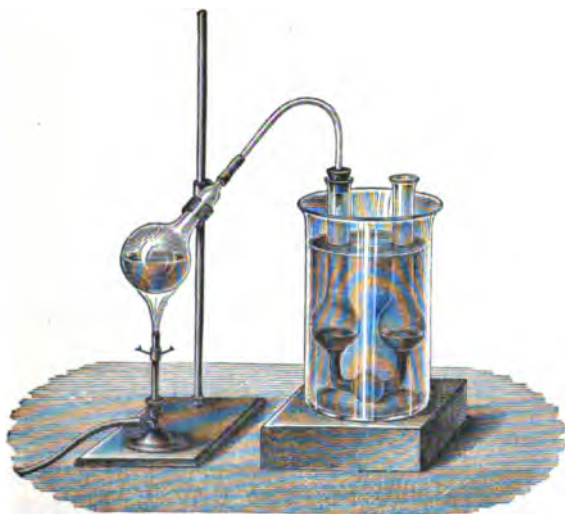


The results obtained by this process are very good (*Paul, Chem. News*, xxi. p. 16).

The process of Bunsen (boiling with concentrated hydrochloric acid, absorbing the evolved chlorine in potassium iodide solution,

titrating the liberated iodine with thiosulphate solution) is the most suitable for the employment of manganese on the large scale, as it directly measures the chlorine produced by it. Yet it is not much employed in factories, because the results obtained by it do not always agree—probably not through any fault of the method, but of its manipulation. Certainly absolutely pure potassium iodide, free from iodate, should be employed; and even in this case the results are not always exact. The process of expelling the chlorine and receiving it in KI does not by itself yield such perfectly correct results as it is generally assumed to yield. Even if the KI and the hydrochloric acid employed are absolutely pure

Fig. 88.



(i. e. on being mixed cold remain colourless for some time), some iodine will be set free if the acid be boiled for some time in Bunsen's apparatus and the steam condensed in a solution of potassium iodide, as in testing manganese it must be. Several drops of thiosulphate solution are required for decolorizing the KI solution; how many, should be discovered by a preliminary test with the same quantity of acid as afterwards employed in the manganese-test; and the quantity of thiosulphate thus required must be deducted from the final result. The apparatus shown in fig. 88 is very convenient for Bunsen's test, since there is no danger of

the iodide solution coming back; but it is best to employ a second receiver filled with KI solution, which need not be emptied if no iodine has been liberated in it.

In all these cases about 0.3 gram manganese is put into the flask, which must hold 50 or 60 cub. centims.; about 25 cub. centims. of pure fuming hydrochloric acid are added, and the neck of the flask is at once connected with the gas-pipe. The receiver has been previously charged with 25 or 30 cub. centims. of concentrated potassium-iodide solution, which must be kept cool during the operation by an external surrounding of cold water. The evolution of chlorine commences directly the flask is moderately heated; the current of chlorine should not be too strong, lest any escape unabsorbed; at last the liquid must be strongly boiled in order to drive over all the chlorine along with the steam and HCl. It is still safer to arrange the apparatus so that a current of air can be drawn through it during the operation, to expel all the chlorine. When the liquid in the flask has become of a clear bright yellow colour, the lamp is removed, and if on removing the gas-pipe from the flask there is a smell of chlorine perceptible in the latter, the experiment must be rejected. The chlorine driven over liberates its exact equivalent of iodine in the KI solution; and this can be measured either by sodium thiosulphate or by sodium arsenite, as we shall see later on when treating of chlorometry. According to the equation



each 87 parts  $\text{MnO}_2$  correspond to 71 chlorine; or  $5 \times 0.087$  ( $=0.435$ ) gram would take up 100 cub. centims. of a decinormal iodine solution; hence, if 0.035 gram of manganese ore is employed for each test, the number of cub. centims. of decinormal thiosulphate or arsenite solution required for decolorizing the liberated iodine indicates immediately the percentage of  $\text{MnO}_2$ . The titration should take place at once, since after long standing the HI liberated by the HCl carried over is decomposed with separation of iodine.

The most usual process of testing manganese ores, at least in England, is that proposed by Levöl and Poggiale, by means of iron. It is based upon the principle employed by Pelouze in estimating nitric acid (Vol. I. p. 173), viz. upon the oxidation of ferrous into ferric salt by the higher oxides of manganese, and remeasuring the unused ferrous salt. The manganese ore is dissolved in the

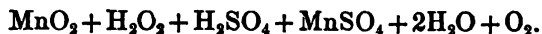
presence of a certain quantity of ferrous salt or of metallic iron, and sulphuric acid, and titrated back by potassium permanganate. The most convenient way of making this test is as follows :— Weigh 1.0875 grm. of manganese ore, ground as fine as possible, and dried some time at  $100^{\circ}\text{C}.$  ; put it into the flask (fig. 89), closed by an india-rubber valve; add 75 cub. centims. (in three pipettesful at 25 cub. centims. each) of a solution containing 100 grams pure crystallized ferrous sulphate and 100 cub. centims. pure concentrated sulphuric acid, diluted to one litre, and standardized on the same day by means of the same 25 cub. centims. pipette, with decinormal potassium permanganate. Close the flask by its india-rubber cork and valve, and heat till the manganese is completely decomposed, leaving a light-coloured residue. On cooling, the valve must act properly, which will be seen by the

Fig. 89.



collapsing of the india-rubber tube. After complete cooling add 200 cub. centims. of water, and titrate with potassium permanganate to a faint pink coloration. Deduct the quantity of permanganate now required from that corresponding to the 75 cub. centims. of iron solution ; the remainder indicates for each cubic centimetre 0.02175 grm., equal to 2 per cent.  $\text{MnO}_2$ .

As a check upon the above process, the analysis may be performed by means of hydrogen peroxide in an acid solution, measuring the oxygen evolved in a nitrometer or in the gas-volumeter described in Vol. I. p. 185. In this case these instruments must be provided with a reaction-flask *a*, fig. 89. The gas-burner A is filled with mercury by raising the "level-tube" until the mercury comes up to tap *e*. The weighed sample is placed in the outer space of flask *a*, and is agitated with dilute sulphuric acid to decompose any carbonates present. Tube *b* is filled with hydrogen peroxide, whose strength need not be known, but which must be in excess. The stopper *f* is put in, and the compression caused thereby is removed by opening the plug of *e* for a moment, and again bringing the mercury to the zero-point of the scale. The flask in this case and later on must never be grasped otherwise than by its neck, to prevent heating it; for very accurate work it is best to place it, before and after each operation, in a dish filled with water of the temperature of the room, until the temperatures are equalized. Then *e* is turned so that *a* communicates with A (the mercury still being at zero); now the flask is inclined so that the hydrogen peroxide runs from *b* into *a*, and it is shaken up, lowering the level-tube to avoid unnecessary pressure. After a very few minutes (not exceeding five) the evolution of gas is finished; the colour of the residue must be light without any dark particles. The latter consist of undecomposed manganese ore, and if such are present the test is lost. Some ores, in spite of the finest trituration, cannot be completely decomposed, and these cannot be analyzed by this method. The reaction is:—



Any prolonged agitation must needs be avoided, as otherwise some oxygen is given off spontaneously from the  $\text{H}_2\text{O}_2$ ; but this does not happen quite so easily in acid liquids, like the present, as in alkaline liquids.

Now the reading is *at once* made. For this purpose the level-tube is placed in such a position that the mercury-levels in this and in the tube A are exactly at the same height; the tap *e* is closed, and in case of an ordinary nitrometer the gas-volume in A is read off now, as well as the thermometer and barometer, reduced to 0° and 760 millims. pressure. In the case of a gas-volumeter the procedure is as described in Vol. I. p. 186, to avoid the neces-



sity of any reduction. Notice, however, must be taken that the reduction-tube in this case is regulated for *moist* gases; or else a special correction must be made for this object.

Each cub. centim. of the oxygen evolved, reduced to 0° and 760 millims., is = 0.003897 MnO<sub>2</sub>.

3. *Carbonic acid* is either estimated gravimetrically by expelling with dilute sulphuric or nitric acid and absorbing in soda-lime, or better and more quickly volumetrically in Lunge and Marchlewski's apparatus, Vol. II. p. 113.

4. *The quantity of hydrochloric acid required for dissolving the manganese ore* is sometimes estimated, as it is very different for the same quantity of MnO<sub>2</sub> indicated by the test, if the composition of the ore varies. If, for example, the analysis indicates 60 per cent. MnO<sub>2</sub>, this might all be present as real manganese dioxide, along with 40 per cent. gangue, and would require much less HCl than if, along with 60 per cent. MnO<sub>2</sub>, 40 per cent. of MnO were present. These are both extremes which do not happen in practice; and on the whole practical wants are satisfied by the above-mentioned custom of the trade, according to which the ore is not paid for in direct proportion to its percentage of MnO<sub>2</sub>, but on a much higher scale; for a rich ore nearly always consumes comparatively less acid than a poor one. The oxides of manganese behave towards hydrochloric acid as follows:—



Besides, any iron oxides occurring in the ore consume acid without yielding chlorine, not to mention carbonates.

Still the quantity of HCl required for decomposing the manganese ore ought to be estimated much more frequently than it usually is. This is done by dissolving a certain weight of ore in a known quantity of hydrochloric acid, in a flask with a reflux-cooler, or, more simply, fitted with a vertical glass tube, 3 feet long, passing through its cork, so that any HCl volatilized by the heating is condensed and runs back into the flask, whilst the chlorine may escape. When the decomposition is quite complete, the

flask is allowed to cool, its contents are diluted, and the remainder of the acid titrated back. This is best done by employing as an indicator the ferric oxide which is always present in manganese ores, and simply adding standard soda or ammonia to the acid manganese solution till reddish-brown flakes of ferric hydroxide are formed, which on shaking do not redissolve.

### *Hydrochloric Acid.*

At first chlorine was always made from manganese ore, common salt, and sulphuric acid, which act as follows:—



Hence a residue is obtained which is a mixture of sodium and manganese sulphate very difficult to utilize. But in the infancy of alkali-making the high price of soda permitted the working of these residue liquors for it, *e. g.* at St. Rollox about the year 1800 (Mactear, *l. c.*). This mode of preparing chlorine is nowadays practised only in laboratories, and in some isolated cases where gaseous chlorine is used for bleaching, and where the difficulty of transit renders the salt and sulphuric acid cheaper than their equivalent of hydrochloric acid. This happens, for instance, at some paper-mills, but is getting less common.

As soon as by the development of alkali-making larger quantities of *hydrochloric acid* became available, this acid was at once made use of; and it is now almost the only source for the bleaching-powder, bleach-liquor, and chlorate of potash of commerce. Only during the last few years other sources of chlorine have been added, *viz.*, magnesium chloride and the electrolysis of alkaline chlorides.

Concerning the *quality* of the hydrochloric acid, we must take account of its concentration and of its impurities.

The *concentration* of the hydrochloric acid is of great importance for the manufacture of chlorine, and mostly so in the case of natural manganese ore, of which the harder descriptions especially are not at all affected by dilute acid, not even at a higher temperature. When, therefore, a certain portion of the HCl contained in the acid has been consumed in the formation of  $\text{MnCl}_2$ , and of free chlorine, the action ceases, although there is still a considerable quantity of HCl present. In the case of ordinary soft manganese ore, the lower limit down to which it pays to go in

the preparation of chlorine may be placed at the point when the liquid contains 5 per cent. HCl; in the case of hard manganese ore in lumps, the operation must very frequently be finished at 7 or 8 per cent. HCl, because the disengagement of chlorine is then too slow even at a boiling heat. It stands to reason that we are incomparably better off if we make a certain quantity of HCl act in the presence of less water than in that of more water. Not to complicate this explanation, we will take no account here of the dilution of the water condensing from steam. Suppose we begin with acid of 36 p. c. HCl and we go down to 6 p. c., we have then utilized  $\frac{5}{6}$  of the acid and lost  $\frac{1}{6}=16\frac{2}{3}$  p. c. If, however, we had begun with acid of 27 p. c. HCl, as often obtained from open saltcake furnaces (Vol. II. p. 174), we utilize only  $\frac{2}{3}$  and lose  $\frac{1}{3}=25$  p. c. If we only go down to 8 p. c., which is much more frequently the case, the comparison is even more unfavourable, for then we lose in the former case  $\frac{8}{3}=22\cdot2$  p. c., in the second  $\frac{8}{4}=33$  p. c.

The utilization of the acid can be carried much further if it is used for recovered manganese—"Weldon mud," as we shall see. In this case a very high strength of the acid is not quite so important, but even here it has a very decided influence on the yield of chlorine.

The *impurities* of hydrochloric acid are of no consequence when employing it for decomposing native manganese ore. Iron, arsenic, &c. are never present in any essential quantity, and do not interfere with the evolution of chlorine. Only sulphuric acid might be quantitatively important: this circumstance does not in any way disturb the process, it simply replaces part of that HCl which enters into combination with Mn; there is a little  $\text{MnSO}_4$  formed instead of  $\text{MnCl}_2$ . Even 2 or 3 per cent. sulphuric acid, which sometimes occurs in roaster-acid, does no harm here.

The case is very different if the hydrochlorine acid is required for the Weldon or Deacon process: here the sulphuric acid is very injurious, as we shall see in the following chapters.

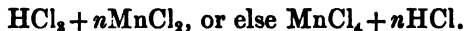
We must bear in mind that even under such circumstances as never occur in practice, viz., with pure manganese dioxide and with a complete utilization of the hydrochloric acid according to the equation



only 50 per cent. of the chlorine is set free. If we consider that

in practice at least  $\frac{1}{3}$  of the HCl remains in the residue, we obtain a utilization of at most 42 per cent. in the shape of free chlorine. But even this figure is much too high: firstly, on account of the dilution by the water condensing from steam; secondly, because pure  $\text{MnO}_2$  is never used, but there is always an excess of  $\text{MnO}$  to dissolve, and frequently also ferric oxide &c. Even in well conducted works the practical yield of free chlorine is only from 30 to 33 per cent. of that contained in the hydrochloric acid.

During the action of concentrated hydrochloric acid on manganese dioxide in the cold a coffee-coloured liquid is formed, which gives off chlorine even at ordinary temperature, but much more on heating, and on boiling passes into a bright yellow colour (caused by the presence of iron) with evolution of all the free chlorine. The brown liquid contains a very unstable higher chloride of manganese. This was always taken to have the formula  $\text{MnCl}_6$ , which was also confirmed by Fisher (Journ. Chem. Soc. 1878, p. 409). Pickering (*ibidem*, 1879, p. 654) assumes the formula to be  $\text{Mn}_2\text{Cl}_6$ ; but this is contradicted by all others. Berthelot (Compt. Rend. xci. p. 251) has made a minute examination of the liquor referred to. It is decolorized only by boiling; on dilution with water it becomes turbid and a hydrate of  $\text{MnO}_2$  is precipitated, whatever may have been the composition of the oxide of manganese dissolved in the hydrochloric acid. Probably the brown liquid is not simply a solution of  $\text{MnCl}_6$ , but its formation requires also free HCl, for a solution of  $\text{MnCl}_2$ , when treated with free chlorine at  $12^\circ \text{C}$ ., absorbs only half as much as pure water. The reaction is accompanied by phenomena of equilibrium, influenced both by the concentration of the acid and the temperature. A sample of manganese dioxide which is completely soluble in concentrated hydrochloric acid, when suspended in dilute acid (1.6 per cent.) yields chlorine even in the cold with formation of a brown liquid; but the reaction is very incomplete. Probably the brown liquid contains an unstable perchlorinated hydrogen-manganese chloride,



Vernon (Proc. Chem. Soc. 1890, p. 58) has proved Pickering's experimental data to be entirely erroneous; the assumption of a compound  $\text{Mn}_2\text{Cl}_6$  must be definitely abandoned, and the formula  $\text{MnCl}_4$  must be retained.

*The Manufacture of Chlorine from Salt, Manganese Ore, and Sulphuric Acid.*

During the first period of manufacturing bleaching-powder, when hydrochloric acid was not yet cheap enough, chlorine used to be made from common salt, manganese, and sulphuric acid. If these materials are mixed in the proportions indicated by theory, *i. e.*



a very high temperature must be employed in decomposing them, as at first monosodium sulphate ( $\text{NaHSO}_4$ ) is formed and only half the chlorine is liberated; hence the heat must be increased beyond  $120^\circ \text{C}$ . (which is not easily done in practice by means of steam), or more sulphuric acid must be employed, according to the equation



This, again, makes the manufacture of chlorine more expensive. The latter proportion would mean 87  $\text{MnO}_2$ , 117  $\text{NaCl}$ , and 297  $\text{SO}_4\text{H}_2$ , and yield 71 chlorine; but as the materials are not pure, about 1 part of common salt, 1 part of ground manganese, and  $2\frac{1}{2}$  parts of vitriol are taken, the latter previously diluted with an equal weight of water, or employed in the state of chamber-acid.

Klason (Ber. d. deutsch. chem. Ges. 1890, p. 334) states that when employing the above-mentioned proportions only 71 per cent. of the chlorine is set free. The course of the reaction must be represented by a different formula, *viz.*:

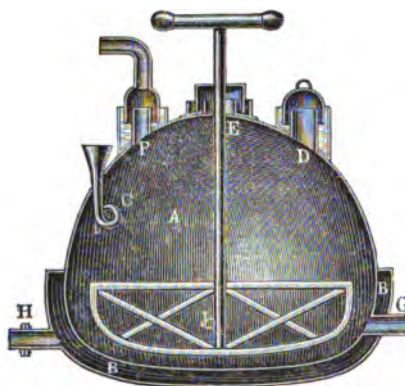


This corresponds to 5 parts of 90 per cent. manganese ore, 11 common salt, and 14 strong sulphuric acid, diluted with its own bulk of water. Thus 95 per cent. of the total chlorine is obtained, and the above proportions are also the cheapest to use.

For preparing chlorine from salt and sulphuric acid, leaden apparatus were usually employed (represented in fig. 90). The principal part is a leaden still; the lower portion of this is surrounded by an iron jacket B B separated by a narrow interval from the still-sides, so that the latter can be heated by steam entering through the pipe H. Sometimes the lower portion of the still was arranged for heating by direct fire, by constructing it as a cast-iron

dish with a rabbet in its upper edge, into which the leaden upper part was cemented. The latter is provided with the charging-hole D for manganese, the funnel-tube C for muriatic acid, the gas-pipe P for chlorine, and the opening E for the vertical shaft of the agitator J. All openings are provided with water-lutes (as indicated), which must be deep enough to prevent any escape of gas at the highest pressure experienced by friction on the pipes or other

Fig. 90.



resistances. Such water-lutes are regularly employed in chlorine-making, because most other joints do not stand, owing to the rapid destruction of screw-bolts, &c. The pipe G serves for running off the contents of the still at the end of the operation.

Apparently, for some decades such leaden stills were exclusively in use, although very often needing repair and quickly worn out. For liquid hydrochloric acid they cannot be used at all, because when heated it quickly dissolves the lead. In No. 5739, 1828, Morfit patented, as an improvement, lining the leaden retorts with glazed stoneware. Gamble's was a much more important improvement (patent, No. 8000, 1839). He abandoned the use of lead, except for the lid, and employed deep stoneware pots with a jacket enclosing an annular space 3 inches thick, in which there was a circulation of hot water, hot solution of salt, or steam. The pot tapered towards the bottom, where it had a discharge-pipe; it was again contracted at the top, so that the lead of the cover could be turned over it and tightened by an iron hoop; between lead and stoneware oil cement was put. These stills were each provided

with an agitator, and accordingly could be employed for ground manganese, salt, and sulphuric acid, or for manganese and muriatic acid, as the lead cover only came into contact with gaseous HCl.

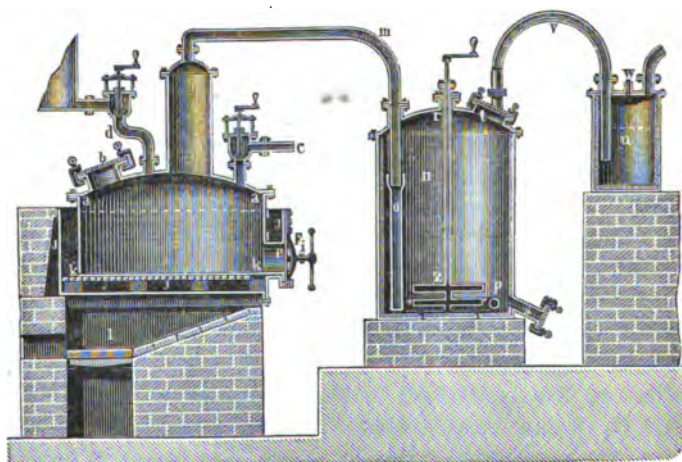
The stoneware apparatus to be described below might also be employed for making chlorine gas from salt and sulphuric acid; but if no agitators are provided, the materials must be well ground and mixed together.

Wurster (Fischer's *Jahresb.* 1887, p. 540) describes chlorine-stills for manganese, salt, and sulphuric acid, consisting of a cast-iron pan with discharging-pipe and a cylindrical leaden hood for the frothing over of the mass. As long as there is an excess of manganese present, the cast-iron is but little acted upon.

The residue from this operation (a mixed solution of manganese and sodium sulphate) is almost worthless; and, as we have seen, this mode of operation is applicable now in rare cases only. The grinding of manganese is also expensive. On the large scale, for a long time past, hydrochloric acid and manganese have been used exclusively; but this cannot easily be done, except at saltcake works, since the cost of packing and carrying muriatic acid is out of proportion to its value; hence the manufacture of bleaching-powder is only possible where the HCl itself is produced. A transition to this is afforded by the process of decomposing NaCl and  $\text{SO}_4\text{H}_2$  in one compartment of a vessel, and allowing the gas to pass into the other compartment, where manganese is suspended in water. In this case the residue from the first compartment might be used as acid sodium sulphate; but the decomposition is incomplete, and the apparatus impracticable. According to Wagner's *Jahresb.* 1857, p. 105, Clément is said to have proposed such an apparatus (when?). Maughan (pat. No. 7039, 1836) was probably the first to act upon manganese directly with the HCl formed in the decomposition of common salt by sulphuric acid. The manganese, in fragments, was contained in a vertical cylinder provided with a grate just above the bottom, and was constantly kept moist by water. The cylinder was enclosed in a jacket in which steam circulated and kept the temperature up to at least  $55^\circ\text{C}$ . The HCl gas entered at the top; the chlorine passed out at the bottom; it was to be washed and then brought to a red heat in platinum tubes (!), and ultimately cooled and conveyed into the absorbing-chambers. A similar apparatus, patented by Seybel,

No. 9310, 1842, is represented in fig. 91. *a a* is a leaden retort, in which salt is decomposed by vitriol; *b* is the man-hole for charging the salt; *c*, a pipe leading towards the chimney, closed by a valve during the decomposition; *d*, a pipe, with a valve, to admit the vitriol; *e*, discharging-pipe for the sodium bisulphate, covered by a leaden lid *F*, held fast by an iron frame, screw-bolt, and arm *i*. *J J* is an iron oil-bath with a perforated false bottom, *k k*, as support for the vessel *a a*. The heat in *a a* was not to exceed

Fig. 91.



166° [?!]. The charge consisted of 1 ton of salt and  $1\frac{1}{2}$  ton of sulphuric acid of spec. grav. 1.71. The HCl escapes through *m* into the manganese-vessel *n*, lined with fire-bricks. The pipe *m* is continued into a stoneware pipe *o*, and this into a hollow ring *p* with several small holes, through which the HCl gas is conducted below the level of the water and the manganese. The latter is from time to time stirred up by an iron agitator *z*, lined with lead, which passes through the gland *r*. *s* is the discharge-hole; *t* man-hole; *v*, gas-pipe. The chlorine is washed in *u* with water and about 5 kils. of manganese; the water can be siphoned off through *w*. *n* is charged with 7 cwt. manganese of 62 per cent. and 11 or 12 cwt. of water; it is worked off in 15 hours. The many practical difficulties of this apparatus are evident; it has hardly ever proceeded beyond the stage of trial.



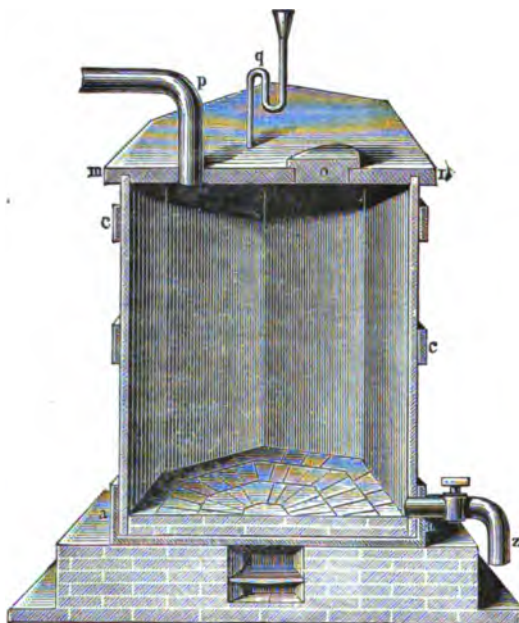
The same principle was again patented by Monod (No. 2147, 1856); he employed a manganese-vessel with a perforated false bottom. Baggs and Simpson once more patented the same thing (No. 1475, 1862).

Dormer (Engl. pat. 5225, 1889) decomposes manganese ore with a mixture of hydrochloric and sulphuric acid, in order to set all the chlorine free, the manganese being converted into sulphate. The latter is treated with calcium chloride, and the solution of  $MnCl_2$  filtered from the  $CaSO_4$ , in order to be subjected to the Weldon process for recovering the  $MnO_2$ . The "inventor" of this process points out that the only extra cost for completely converting the  $HCl$  into chlorine is the sulphuric acid [certainly!].

#### *Manufacture of Chlorine from Manganese Ore and Hydrochloric Acid.*

The manufacture of chlorine from manganese and hydrochloric acid cannot be carried out very well except in vessels of stone or stoneware. At first these were often built as shown in fig. 92. They were composed of eight stone slabs, kept together by a cast-iron bottom piece with a flange *a*, midway and toward the top by hoops *c c*, and at the top by the stone cover *m n*. The bottom was paved with a double course of fire-bricks, as a protection against the acid. The hole *o* admitted the charge of manganese, *q* that of the acid; *p* carried off the chlorine gas; *z* was for the discharge of the waste liquor. A small fireplace beneath the iron bottom, as in the figure, or a steam-jacket served for the heating. These apparatus are said to have sometimes exploded—which, however, cannot have been a consequence of their construction, and may happen with any construction through an excess of pressure. Neither are the joints more difficult to keep tight than others; but probably the iron bottom was not sufficiently protected from the acid by the brick pavement; and the heating of the apparatus by an open fire from beneath must have been very imperfect, and the evolution of chlorine but slow. As there was no grid provided, much manganese must have been lost, especially as, in the absence of an agitator, ground manganese could not be used to advantage, though it seems to have been used. A still patented by Boyd (No. 1359, 1853), made of cast iron with a fire-brick

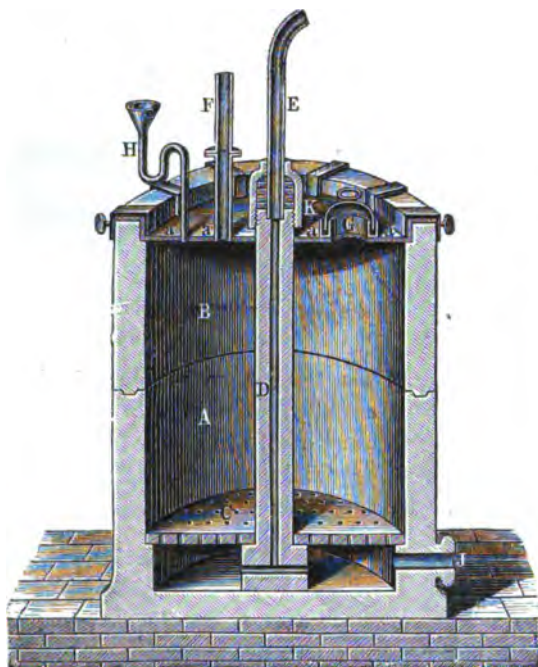
Fig. 92.



lining, set in mortar of pipeclay, ground pitch, sand, and boiled oil, is quite unworkable.

A much better chlorine-still is represented in fig. 93. The apparatus, made of scooped-out blocks of sandstone, is about 6 feet 6 inches high and 3 feet 3 inches wide, hence made in two pieces (A and B), which are rebated together in the middle and joined with clay and boiled oil. A also includes the bottom; the thickness of the sides up to 6 inches above this is a little more than higher up, so that a recess of 2 inches all round is formed, on which rests the perforated plate C, on which the manganese (in pieces) is placed. D is the steam-pipe made of sandstone, connected by E with the main pipe; the steam can only escape below the false bottom, by the perforations of which it is well distributed. The top of this still was made of lead (stone would be much better), and was provided with openings for the chlorine-pipe F, the man-hole G, the acid-funnel H, and the steam-pipe E. The lower opening, J, closed by a wood plug, serves for discharging.

Fig. 93.



A peculiar form of still was patented by Lee (No. 9041, 1841), viz. shallow stone troughs covered by shallow brick arches, in the shape of an oven. They stood on an open foundation beneath, and were heated from the top through the arch by an open fire. In order to make the tops gas-tight, they were covered with a mixture of fireclay, ground fire-brick, and common salt. Evidently in these ground manganese was employed; and cracking the bottom was avoided by not heating it. But in this way these stills must have been very imperfectly heated; and they were soon given up again, as appears from the fact that Mr. Lee's partner, W. W. Pattinson (No. 11290, 1846), patented a new form of still, an improvement of which was the subject of a fresh patent (No. 14056, 1852) and was in use at the Felling works near Gateshead up to the time of the introduction of the Weldon process. This apparatus already exhibits all the parts of modern stills, and was, moreover, specially protected against cracking and against dilution by condensed steam.

Figs. 94 and 95 show its first construction. *aa* is a circular

Fig. 94.

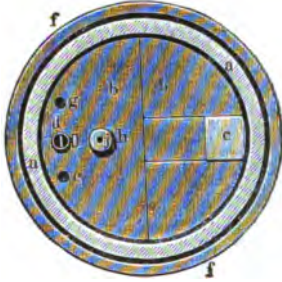
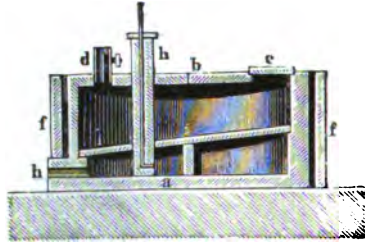


Fig. 95.



still, made of stone, *b* its top; *c*, man-hole; *d*, chlorine-pipe; *i*, false bottom (grate); *e* and *g*, holes in the top for introducing the acid and gauging the height of the liquor; *h*, aperture admitting the stone steam-pipe; *ff*, double iron jacket for heating the still from without. In the later construction (figs. 96, 97) the

Fig. 96.

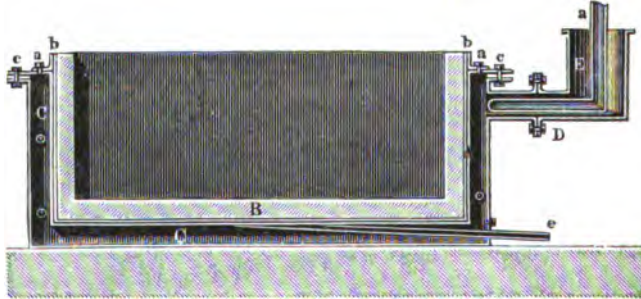
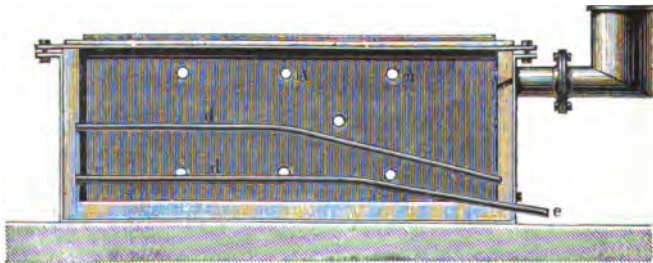


Fig. 97.

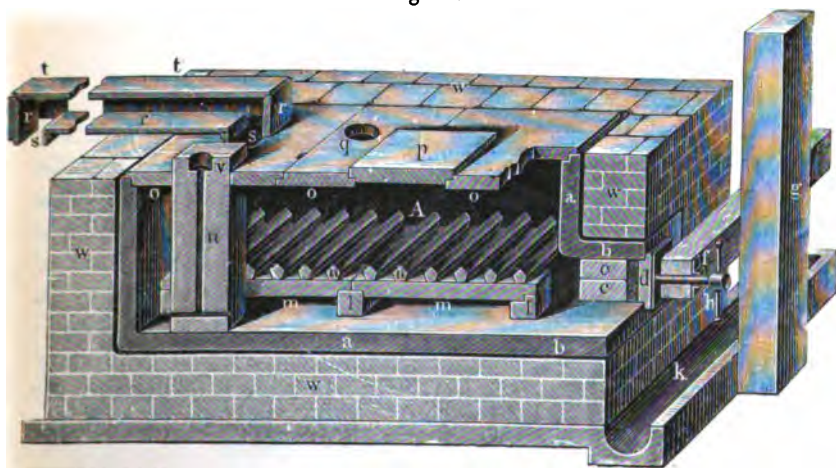


inner iron jacket A is perforated by a number of holes ; the stone vessel B is 6 inches higher, and its projecting portion is surrounded by the iron ring *aa* which leaves a small caulking-space *b*, and has a flange which is bolted to the flanges of the iron jackets A. The joint is made by india-rubber washers and melted lead. The small iron reservoir E communicates through D with the space between the stone and the iron jacket, and with the annular space C between the two jackets ; the steam-pipe, *d*, coils several times round the stone still and comes out at *e* (fig. 97, which represents the jacket without the still). Into the vessel E hot coal-tar, boiled down to the consistency of pitch, is poured till the whole space C C is filled ; and this is always kept hot by the steam-pipes ; so that the still is heated from without, and at the same time its cracking prevented by the uniformity of heating. Even if the stone should still get cracked, the work may be continued, since the tar prevents the acid from getting out. This construction is somewhat expensive, especially from the necessity of making the inner vessel from a single block of stone ; and therefore its use has not been very widely extended.

Lister's patent (No. 69, 1854) leaves spiral channels within the sides of the still itself, for heating it by means of steam or hot air —an unpractical construction.

At several German works there are found chlorine-stills of the shape represented in fig. 98. A is a square box, consisting of the

Fig. 98.



proper still *aa* and the brick jacket *w*. The still *aa* is cut out of a single block of sandstone, and covered with a slab of the same material ; where such large blocks cannot be had, the stills are composed of several pieces. In any case the sandstone is boiled in tar till it absorbs no more of it. The sides are 6 to 8 inches thick, 6 ft. 6 in. long, 3 ft. 6 in. wide, and 2 ft. 6 in. high. The brick jacket is 10 inches thick, and leaves between itself and the still an inch space, which is filled with melted pitch. A little above the bottom a grate *nn*, consisting of sandstone, lies on the sleepers *ll* and *mm* ; upon this the manganese ore (about 10 cwt.) is charged through the man-hole ; the lid of the latter is made tight with red lead, pipeclay, and boiled oil. The acid arrives through the pipe *g*, the steam through the sandstone column *uv*. A sandstone flue, *rst*, conveys the chlorine gas to a second still and then to the chambers. The wide neck *bb* serves for discharging the residues into the shoot *k* ; it is closed by bricks coated with moist clay, upon which the sandstone lid is placed and made tight with clay. By means of the wooden post *g*, the movable crossrail *f*, and the screwbolt *h*, the lid *d* is pressed tightly against the still ; it is protected from fracture by an iron plate. The acid is run in by a lead box and siphon, fig. 99, the longer

Fig. 99.



limb of which is cemented into the hole *g*. When the acid has risen to the dotted line *a* the siphon begins to run, and empties the whole vessel, which usually holds a carboy full of acid. [This is a very clumsy contrivance ; why should the acid first be filled into fragile carboys and one such run in at once, instead of running it in directly from a tank and regulating its flow by an earthenware cock ? The grating *nn* is also very unsuitable, especially liable to break ; so is the gas-flue *rst*, which is in every way inferior to good stoneware pipes ; and there is no opening for gauging the height of the acid, which has to be done through the man-hole !]



The stills mostly employed in England for the last forty years, which even since the introduction of Weldon's process are still required for decomposing the fresh manganese, are shown in figs. 100 to 103; but of course there are differences in detail. The corners, especially in Lancashire, are often, and on the Tyne always, made in a somewhat different way, viz. with feather-and-groove joint (as shown in the case of condensers in figs. 106 to 108, Vol. II. p. 337). Fig. 100 shows a still seen from above; fig. 101, in front; fig. 102 a section through A B, and fig. 103 a section through C D, of the plan, fig. 100. The stills are built of flags of

Fig. 100.

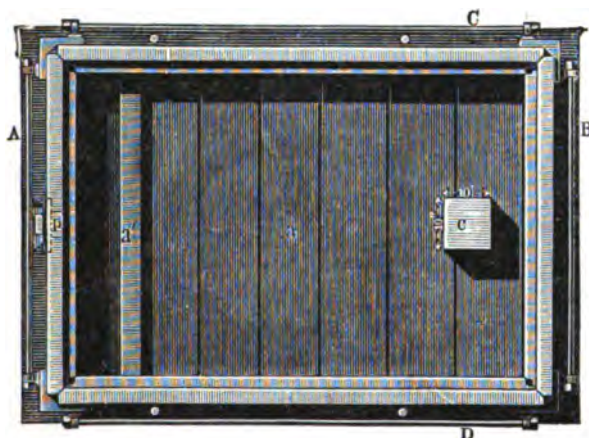


Fig. 101.

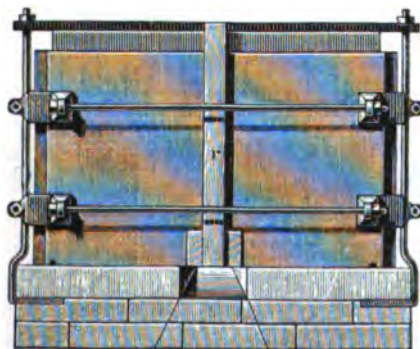


Fig. 102.

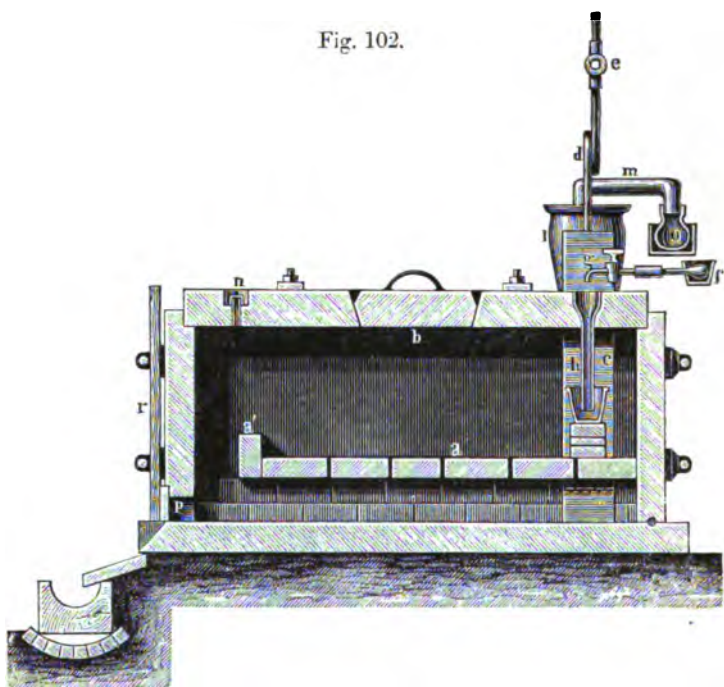


Fig. 103.

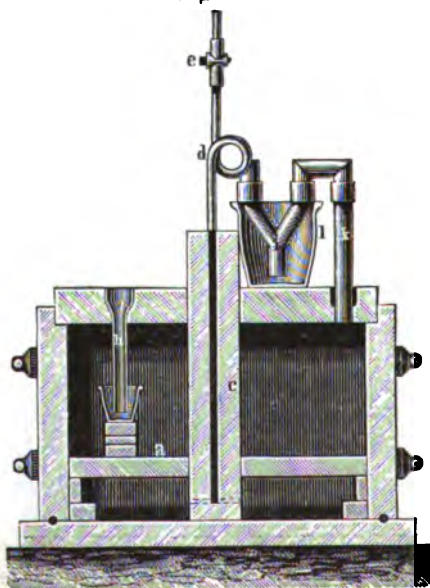




Fig. 104.

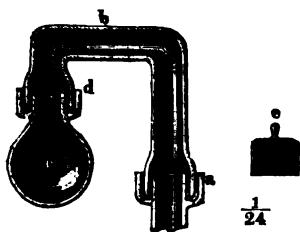


Fig. 105.

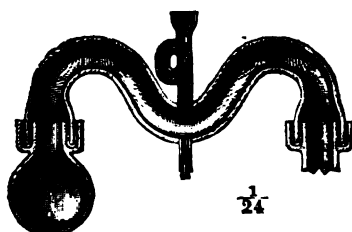
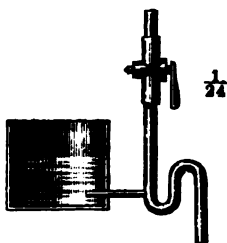


Fig. 106.



siliceous sandstone from Halifax, in Yorkshire, Felling-on-Tyne, &c. If the stone is at all porous, it is first boiled in tar; or the still, after being put together, is filled with tar, and this is boiled for some time by means of steam. Stills made out of a single block are occasionally used, but always of smaller dimensions than those drawn. In the construction as shown in the diagrams the joints of the side flaps with each other and with the bottom flap are made tight by india-rubber cord about  $\frac{3}{4}$  inch thick; when feather-and-groove joints are employed, the well-known tar-and-fireclay cement is used. The manner of binding together the flaps by iron ties can be seen from the figure; this, as well as all other details of construction, has been exactly described in the case of acid-tanks (Vol. II. *l. c.*). The stills must have a very substantial foundation, lest they should settle down from their weight, which always causes leakages. The foundation cannot be set with lime-mortar, but only with tar and sand. The bottom stone is 9 to 12 inches, the sides and top are 6 to 8 inches thick; the top may consist of two pieces. The parts peculiar to chlorine-stills are as follows:—First a sandstone grate *a*, consisting of sleepers placed close together, as their rough sides do not touch closely enough to prevent the acid getting through; this permits employing

manganese ore even in the state of fine powder. Sometimes the front sleeper *a'* is placed upright as drawn, in order to facilitate the circulation of the acid ; but then care must be taken on charging the manganese ore through the man-hole, lest any of it fall over the sleeper *a'*. The grate is pierced so as to allow the passage of the square stone or stoneware pipe *c*, of 1-inch bore, which below the grate has three side openings ; it is joined on the top, by cement, to the lead pipe *d*, which beyond the cock *e* is continued into an iron steam-pipe, branching off from the main pipe. The loop of the lead pipe *d*, after the steam is shut off, at once fills with condensed water, as the cock *e* is never quite tight, and thus preserves the latter for some time from corrosion by the chlorine gas, which rises up in the steam-pipes when the steam is shut off. On starting the steam again, the water is blown off into the still. But it takes a little time for enough condensed water to collect to protect the cock against chlorine ; and in the meantime the cock is strongly acted upon. A complete cure for this is afforded by the contrivance shown in fig. 106. Here the bend of the steam-pipe is connected by a small leaden branch pipe with a lead box of 12 inches square and height, in which water stands almost up to the level of the bend of the steam-pipe. The branch pipe is closed at the end, up to a pin-hole, through which in the state of rest the bend is filled with water. On starting the steam it blows the water into the still ; a little also blows through the pin-hole into the water of the lead box, condenses there, and replaces that blown away before. When the steam-cock is shut, the water instantly runs through the pin-hole back into the bend, and protects the cock above from the chlorine gas below. In this way the cocks last five or six times as long as with the ordinary arrangement. The hydrochloric acid runs from the main pipe *f*, through the branch and cock *g*, into the earthenware pipe *h*, which stands in a pot, so that an acid lute is formed and no chlorine gas can get out. The opening *n*, closed by a hydraulic lute, serves for gauging the height of the acid. The chlorine gas escapes through the 3-inch earthenware pipe *k*, the connexion and disconnexion of which with the main gas-pipe *o* is here effected by a very simple apparatus. The pipe *k* is continued into a Y-shaped pipe *i*, open at the bottom and standing in a large earthenware pot *l* ; the other limb of *i* is connected by the bow *m* with the main pipe *o*. When water is poured into the pot *l* above the level of the point of junction of the

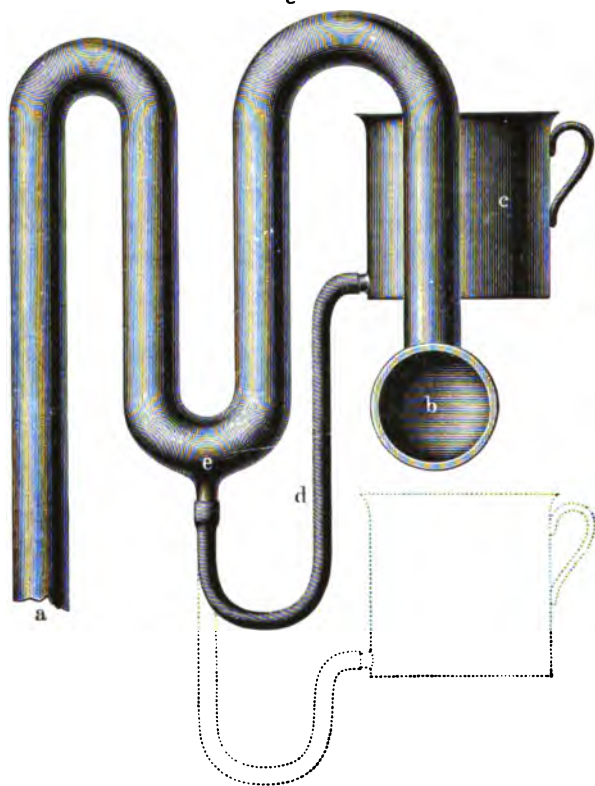
two limbs of *i* (as in fig. 103), the still is cut off from the gas-main, and can be cleaned and charged; but if the water is partly run out of *l* by a siphon or cock, the gas can pass through and the still communicates with the gas-main. The lower end of *i* must always be luted by water. In the place of this very simple and efficient contrivance many others are employed, often causing a loss of gas in handling them. One of the simplest and most frequent is shown in fig. 104. To each branch pipe *a* there corresponds, on the main pipe *c*, a water-lute, formed by two concentric rings of 4 or 6 inches depth; and a similar water-lute is also made on *a* itself. If the still is to be connected with the gas-main, the bow *b* is put on; if it is to be cut off, the bow is taken out and the cap *e* put on. But during this change gas always comes out of the main-pipe. Another simple cut-off, which is not subject to this drawback, is shown in fig. 105. If the still is to be cut-off, water is poured through the funnel into the bent down portion of the connecting-pipe between the still and the gas-main, till the connexion is interrupted; if it is to be made again, the water is removed from the pipe by pulling out the bottom plug.

A good arrangement is also that shown in fig. 107: *a* is the pipe coming from the still, *b* the main. The bucket *c* is connected by the india-rubber tube *d* with the lower bend of the connecting-pipe *e*. In the high position of the bucket, as shown in the diagram, bend *e* is sealed by water. If *e* is lowered into the position indicated by a dotted outline, the water runs from *e* into *c*, and the way from *a* to *b* is free.

Figs. 100 and 102 also show the discharging-hole *p* for the manganese-liquor, which is always mixed with much mud. Ordinary cocks or valves are not applicable here, for reasons easily understood. The discharging-hole has the shape of a D lying on its side, and goes down to the bottom, which is sometimes inclined towards it; it is closed by a plug of wood wrapped round with brown paper and driven in with a hammer; but in the drawing another kind of fastening is indicated, viz. a lath *r* reaching down between the tie-rods and the stone, which squeezes the plug against the hole *p*. These running-off holes are a great nuisance; they might be closed much more safely, *e. g.* in the way shown in fig. 98, or still more so in that to be described for Weldon's stills; but that is not quite so easy here, because they have to be very frequently opened (every 24 or 48

hours). But it might be arranged to employ a large stoneware cock, say 3-inch bore, as in the Weldon stills, for daily use, and a man-hole only to be opened now and then. Sometimes the

Fig. 107.



pressure within the still forces out the plug and with it all the contents of the still. In order to catch the liquor violently shooting out in this case, and also in the ordinary discharging, the stills are placed in two rows, between which runs a gutter for the liquor; in front of the stills a pavement is made of tightly-joined flags, with considerable descent to a gutter in the middle. The latter is either made of long hollowed-out stones, or, as it is very difficult to keep the joints tight against the hot acid liquor, it consists of a single large balk scooped out in the shape of a gutter. If several such balks are to be connected lengthways (and the same holds

good of the joints of stone gutters), the joints are half-lapped and made as tight as possible with hard pitch, &c. The balks are made of American pitch-pine, 2 feet thick and 50 to 60 feet long, with a 12-inch gutter scooped out; they are laid with sufficient fall to convey the liquor quickly into the mud-well, where the clear liquor is separated from the mud. In order to be quite safe against any leakage through the gutters, which unavoidably causes settlings and leakages of the stills, and may even damage the stability of the building, sometimes an inverted arch of fire-bricks set in tar and fireclay is made underneath the gutters. All this is saved when the stills only serve for working the manganese ore destined for replacing the unavoidable loss in the Weldon process; for then they are placed at a suitable height to run their contents straight into the Weldon still by means of a 3-inch stoneware pipe and cock.

Exceptionally, stills are provided with a jacket of stone or brick-work, in order to heat them by steam from without and save some of the steaming within. The latter cannot be avoided entirely, because the heating through the 6 inches of stone is never sufficient; but the outside heating goes some way, and prevents to some extent the dilution of acid by condensed steam; but, on the other hand, cracks and leaks of the inner still are only perceived when they have gone very far and are difficult to repair. This also holds good of a brick jacket with a layer of puddled clay between it and the still for the purpose of preventing the radiation of heat and making any leakages harmless. They really do not do this; for the jacket itself, whenever the acid gets to it, is soon perforated, and then only prevents the discovery of the leak.

All parts of the still, wood, iron, lead, or stone, are well painted with coal-tar, and this paint is frequently renewed; otherwise they are soon wasted away, more especially the ironwork.

On laying out a factory, attention must be paid to giving fall to the hydrochloric acid from the condensers, or from the acid tanks, to the main pipe *f* and thence to each still. The acid-pipes are made of stoneware, joined by sockets and cemented with tar and china-clay or boiled oil and pipeclay. Very suitable, indeed, is the arrangement described in Vol. II. p. 414, consisting of an india-rubber ring round the pipe within the socket, instead of cement. The pumping of hydrochloric acid is avoided whenever possible; the contrivances serving for this purpose are described in Vol. II.

p. 401 *et seq.* Only at very small works is it possible to collect the acid in carboys and charge it by hand into the stills.

*Stills made of stoneware* were formerly very generally employed, and are so even now in bleach-works and paper-mills bleaching by gas; in France they are found even at very large works. If they are to be at all serviceable, the greatest care must be taken in selecting the clay and manufacturing them, even more so than for hydrochloric-acid receivers; and the remarks made in Vol. II. p. 342 hold good even more absolutely in this case. They are made of various shapes. That shown in fig. 108 is intended for manganese in lumps, which is charged after lifting off the top *aa*, resting in a water-lute; *b* is the acid-funnel, *c* the water-lute for the gas-pipe. The shape most usual in France and partly in Germany is shown in figs. 109 and 110: they hold about 45 gallons. The two smaller necks serve for introducing the acid and taking away the gas; the large central opening serves for suspending the stoneware sieve, which is covered by the lid *b*. The wash liquor is siphoned off through one of the small necks. The holes in its lower part are of about  $\frac{3}{8}$  inch diameter; in the upper part there are two larger holes for lifting out the whole sieve by means of specially shaped tongs. The sieve is filled with about 1 cwt. of manganese ore in small pieces; mostly the acid has already been poured into the jar; and the sieve is now suspended and the lid put on immediately and made tight by clay, boiled oil, and Stockholm tar. These jars are always heated from without, four or eight of them being placed in a wooden box lined with lead or a box made of bricks set in cement; this acts as a water-bath, heated by steam; or it is filled with a calcium-chloride solution and heated by a steam-coil; or the box is left empty and the steam heats the jars directly. At the end of the operation the still-liquor is drawn off by a siphon, or by a discharge-pipe passing through the steam-jacket. These small stills in proportion to their turn-out require much manual labour; but they are cheaper than stone stills, and give a very good yield of chlorine from the acid, as this is not at all diluted by steam. The usual charge of acid is about 3 cwt.; there should always be some manganese left behind so as to waste as little acid as possible. In such stills only 6 to 10 per cent. of the acid is lost in the still-liquor, against 30 to 50 per cent. in stone stills; hence where hydrochloric acid is valuable, the stoneware stills pay better, in spite of the

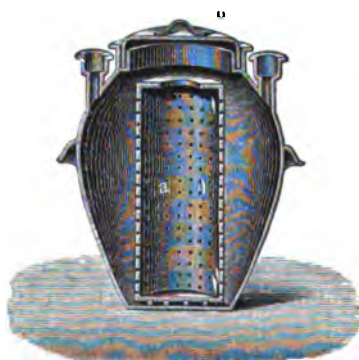
Fig. 108.



Fig. 109.



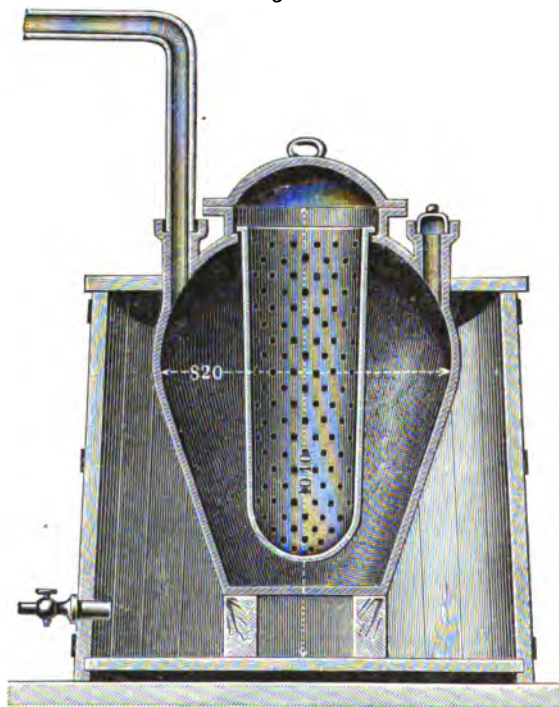
Fig. 110.



increased labour. In the south of France they have replaced the former stone stills (Ballard, 'Rapport du Jury International,' 1868, vii. p. 48); but there are also examples of the contrary, especially in Germany.

Fig. 111 shows such an earthenware still of a capacity of 75 gallons, placed in a wooden trough serving as a steam-bath.

Fig. 111.



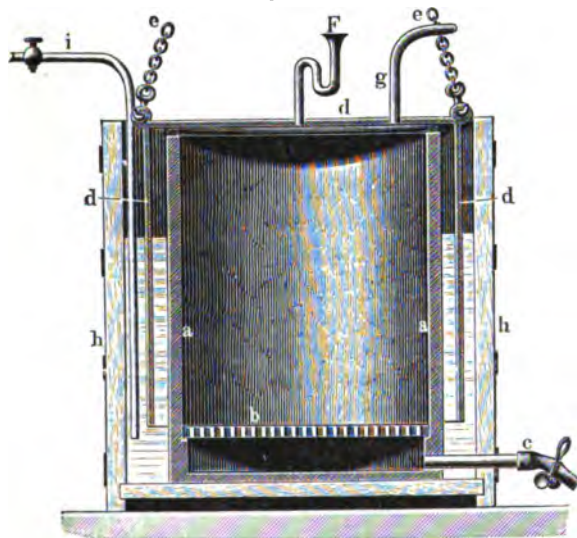
Count Montgelas (Engl. pat. 10009, 1886) describes a chlorine-still for small factories, which contains nothing but generally known features.

An excellent kind of chlorine-still, which I can recommend very much for use at such works where chlorine must be made and consumed on the spot (not, of course, for commercial bleach or chlorates), is that shown in fig. 112. It can be made considerably larger than the earthenware stills made in one piece. An earthenware cylinder *a*, open at the top, is provided with a false bottom *b* and a discharge-pipe *c*. It is covered by a bell *d*, which is usually



made of lead, but might also be made of stoneware; this bell is suspended by the chains *e e* on pulleys, with balance-weights, and

Fig. 112.



is therefore easily moved up or down. The cover of *d* is provided with the acid-funnel *F* and the gas-pipe *g*. The whole stands in a wooden tub *h*, three quarters filled with water, which can be heated by means of the steam-pipe *i*. This water serves both as a heating bath and as a hydraulic seal for the bell *d*. As the joint between *d* and the edge of the stoneware cylinder is provided with an india-rubber ring, very little chlorine can get into the water outside; but as this water is heated, it will not dissolve the chlorine. The charging with manganese ore and discharging of the insoluble residue is done after raising the bell *d*.

The *pipes* for conducting chlorine gas are usually made of lead, but may just as well be stoneware if they are joined by a permanently somewhat soft and elastic cement; in this respect oil-cements are better than tar and fireclay. The pipes ought to be long enough to cool the gas, and to condense any steam and  $\text{HCl}$  carried along before the gas gets into the bleach-chambers. They are made to descend towards a collector of stoneware or lead placed near the chambers, from which the condensed acid water runs off, either from time to time or continuously, through a swan-neck pipe. Sometimes these collectors are filled with man-

ganese ore (but never with limestone!). In colder climates the pipes should be protected by a light roof to save them from being cooled down too much in winter; otherwise they may become plugged up by the formation of chlorine hydrate (p. 264). Lead pipes must be so laid that they may expand and contract with the changes of temperature.

The *work* that goes on with the large stone stills is as follows:—The still, properly cleaned from the previous operation by lifting off the grates and rinsing it out with water, is put right again by stopping up the discharge-holes and putting in the grate-sleepers. It is then charged with the requisite quantity of manganese; say 6 to 10 cwt., according to its size. The manganese ought to be in pieces not exceeding the size of a hen's egg, and less. The man-hole lid is put on and the joint made good with wet clay. This, unless it is always kept moist, cracks and allows gas to escape; it must consequently be watered from time to time, as well as all other clay joints and water lutes; and for this purpose no still-house ought to be without a water-pipe and hose long enough to reach every still. A better cement, but dearer, is made of pipeclay and boiled oil, which is generally used only for permanent joints. Tar and fireclay is not very suitable for this purpose, as it becomes too hard. Then hydrochloric acid is run in till the still is three quarters full, which is tested by a gauge-rod through the hole provided for this purpose. At first the acid is run in quickly, but afterwards, when more chlorine is being evolved, more slowly; so that it takes several hours before the still has got its charge of acid. The evolution of chlorine begins at once, without applying any heat, and the more briskly the more concentrated the acid is. The concentration should be as high as possible; for as the loss of HCl in still-liquors is to a great extent connected with their bulk, a certain bulk of still-liquor always containing about an equal quantity of free acid, much less acid is lost if it was originally concentrated than if it was weak. This proportion becomes still more unfavourable for weak acid from the fact that with the latter more steam must be blown in, which again dilutes the liquor with condensed water. The lowest strength of acid allowable for chlorine-making is  $18^{\circ}$  Tw.; but at this strength about 50 per cent. of the acid is found in the still-liquor, whilst factories working with acid of  $30$ – $34^{\circ}$  Tw. only lose from 25 to 30 per cent., and still less with indirect heating (comp. p. 281). It is true that this

loss is not of any great importance when the still-liquor is first passed through a Weldon still, where its free acid is utilized in the end.

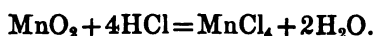
The evolution of chlorine continues for some time, say 8 or 12 hours, without any heat being applied; but after that, to supply the necessary heat, steam is usually blown in. This is done at intervals, seldom continuously, because the temperature would be apt to rise too much. On the Tyne it is a common rule to steam for ten minutes every hour. Care is required lest by too violent an evolution of gas the water be thrown out of the lutes and the gas escape from all the joints of the stills, pipes, and chambers. Hence the stills should not all be steamed at the same time, but alternately—*e. g.*, in a set of 12 stills, two at a time for 10 minutes, so that the turn of the first two comes round again an hour after. Steaming in excess moreover causes much water and HCl to get into the gas-main, and, in spite of collectors, also into the chambers; and thus a single mistake of this kind may spoil a whole chamberful of bleach, or at least prevent it from getting up to full strength. At the same time such neglect creates an intolerable nuisance to the whole neighbourhood, and that in a far higher degree than any escape of hydrochloric, nitrous, or sulphurous acid.

By the successive steamings the temperature of the contents of the still gradually increases; but it ought never to exceed 90° C., because otherwise too much water and HCl escape. When the gas has been driven off as much as possible, the steaming is stopped, the bottom plug is knocked out, and the still then empties itself in a few minutes. This is done once in 24, 36, or 48 hours; the longer the contents of a still can be kept in, *i. e.* the more still-room is provided, the more chlorine will be got from a certain quantity of acid, and the less free chlorine will be present in the still-liquor. Nevertheless there is always enough chlorine present to produce a fearfully suffocating stench on discharging the hot still-liquor. Hence in many works this operation used to be performed between three and four o'clock in the morning, when there is least life stirring in the streets and houses—certainly a very unsatisfactory evasion of the difficulty. Some other plans have been tried, *e. g.* covering with boards the gutter and the mud-well into which the liquor first runs, and drawing off the gas into a brick tower fed with milk of lime. This is a considerable step in advance, but not

quite sufficient. There still remains the enormous contamination of all sewers, watercourses, &c. into which the still-liquor runs. All this is avoided in the Weldon process, where by suitably placing the stills the acid still-liquor is run immediately into the large mud-stills and does not come into contact with the atmosphere.

Frequently the manganese ore is not all decomposed in one operation; in this case, after opening the man-hole, about half the usual charge of manganese is put in, and the still cleaned out only after the second operation. This is especially necessary with the harder descriptions of ore.

In the chlorine-stills the first reaction is (p. 282) :



The perchloride,  $\text{MnCl}_4$ , which yields a dark brown solution, is not stable even at the ordinary temperature, and quickly decomposes into  $\text{MnCl}_2 + 2\text{Cl}_2$ ; but this decomposition is only completed at a little below  $100^\circ \text{C}$ . Accordingly, for 100 parts of pure  $\text{MnO}_2$ , or an equivalent quantity of manganese ore, almost exactly 170 dry  $\text{HCl}$  or about 530 acid of  $32^\circ \text{Tw}$ . ought to be consumed; actually at least 10 per cent., frequently 100 per cent. more are used, for the reason above given:—*i. e.* the maximum with hard and low strength manganese, weak acid, and direct steaming; the minimum under the reverse conditions (pp. 281 and 304).

The *still-liquor* must be daily *tested for free acid*. This can be done with sufficient accuracy by titrating a sample with standard soda solution and taking as the end of the reaction the occurrence of flakes of ferric hydroxide which do not dissolve on agitation. In earthenware stills heated from the outside it is possible, with prolonged heating, to go down to 5 per cent.  $\text{HCl}$  in the liquor. In ordinary stone stills, heated by open steam, 6 per cent.  $\text{HCl}$  is excellent work, but 8 to 10 per cent. is not unfrequently met with.

### *Drying and Purifying the Chlorine Gas.*

In the ordinary manufacture the chlorine gas is only partially freed from water by means of long pipes (p. 303), but it is not directly dried. This cannot be avoided in the Deacon process, as we shall see in the chapter dealing with it. In some special cases the gas must be dried even more carefully than is required in the Deacon process; *e. g.*, when it is employed for the manufacture of anhydrous tin perchloride or of liquefied chlorine. For this object

it is passed through a coke-tower fed with strong sulphuric acid, or through a Lunge-Rohrman plate-tower (Vol. II. p. 382).

In recent years the chlorine gas has been more carefully dried than was formerly usual, even for the manufacture of bleaching-powder, and this is decidedly rational, as will be seen later on from my experiments. If this cannot be done by sufficient air-cooling, it is achieved by cooling the pipes from without by a stream of water.

*Purifying chlorine.*—Weldon (patent No. 2698, 1871) proposes purifying the chlorine gas by a mixture of magnesium chloride and quicklime or by common salt. Hargreaves (pat. No. 3192, 1871) proposes to deprive it of HCl by lime, magnesia, or manganese ore (the latter had been employed long before, comp. p. 303), or to make an impure bleaching-powder and obtain pure chlorine by decomposing that. Neither of these processes seems adapted for the ordinary manufacture of chlorine, but only for that obtained in a dilute state and containing much acid.

*The concentration of dilute chlorine gas* has been frequently proposed, usually by passing it through a milk of calcium or magnesium carbonate, in which case first hypochlorous acid and then free chlorine is formed; sometimes even by absorbing the gas in milk of lime and setting it again free by dilute hydrochloric acid. This has formed the subject of various patents, *e. g.* Hargreaves (No. 3192, 1871); Weldon (662 & 2044, 1872; 2449, 1873); Deacon (3309, 1872).

Loesner (Germ. pat. No. 82437) prescribes obtaining strong chlorine from dilute gases by absorbing it in liquid organic substances, preferably ortho-nitrotoluene, which at the ordinary pressure absorbs up to 11 per cent. chlorine, and gives it off again at a higher temperature or under diminished pressure. It is unnecessary to employ pure ortho-nitrotoluene; a mixture of the isomeric nitrotoluenes will effect the purpose.

*Chlorine hydrate*, according to Heinzerling and Schmid (Germ. pat. 45620), is obtained from dilute chlorine by passing it into water cooled down to 0° C., or into cooled solution of NaCl, &c. The solid chlorine hydrate is separated from the solution, and by heating it strong pure chlorine is obtained.

### *Liquefied Chlorine.*

Since chlorine gas is condensed to a liquid by cooling down to

-34°, or at ordinary temperatures by a pressure of about 6 atmospheres, and since the fact has been long known and technically applied that dry chlorine does not act upon iron, the possibility of obtaining liquid chlorine by cooling or compression and of sending it out in iron bottles could never be doubted. Considerable time elapsed, however, even after other liquefied gases, especially carbon chloride and sulphur dioxide (Vol. I. p. 289), had become articles of commerce on a large scale, before manufacturers dared to treat chlorine in the same way, dreading its fearfully suffocating properties and its corrosive action, which is at once manifested in the presence of moisture.

Already the invention of bleaching-powder, as we shall see, had the object and effect of converting chlorine into a form in which it can be carried to a distance; 1 vol. of bleaching-powder giving out more than 100 vols. of chlorine. Thus this powerful agent could be employed at a great distance from those localities which had the monopoly of its economical manufacture, viz. saltcake and Leblanc-soda works. But bleaching-powder can only in those cases be employed as a carrier of chlorine to distant parts where the action it is to fulfil can be brought about by the bleaching-powder itself, or by the assistance of the carbonic acid always present in the atmosphere. Whenever it is necessary to liberate the chlorine from bleaching-powder by an acid which itself must be bought and carried for a long distance (only sulphuric and hydrochloric acids can be thought of here), this operation is mostly much more expensive than the evolution of chlorine by means of manganese ore, and it can hardly ever be carried out for industrial purposes. Least of all can it be thought of in countries very far removed from the industrial centres, where the acids can no more be manufactured than the chlorine itself, *e. g.* for the gold extraction in South Africa. To provide for such cases, and also in more industrial countries in cases where comparatively small quantities of chlorine have to be employed, has been the object of the new industry of liquefying chlorine and sending it out in iron bottles, 400 volumes of chlorine gas being condensed to 1 volume of liquid.

Vautin (Engl. pat. 8820, 1887) liquefies chlorine by filling a receiver, made of a material resisting the chlorine, with that gas and forcing air into it, until the chlorine is liquefied by compression.

Heinzerling (Germ. pat. 49280) liquefies the gas by cooling down to  $-30^{\circ}$  or  $-50^{\circ}$ .

Hannay (Germ. pat. 49742) makes liquid chlorine from chlorine hydrate (pp. 264, 307), which is heated in a closed funnel-shaped lead-lined vessel, where the water separates from the liquid chlorine; the latter collects in the contracted lower parts, where it percolates through strong sulphuric acid (for the purpose of drying it) and then runs into the iron stock-bottles.

The patent of the Badische Anilin- and Soda-Fabrik, which has been the first to manufacture this article on a large scale (No. 13070, 1888), shows two different apparatus. In one of these, fig. 113, two vessels, A and B, are connected at the lower portion. B and the lower portion of A are filled with sulphuric acid (in which chlorine is hardly soluble), the upper portion of A with petroleum, which floats on the acid and reduces its effect on the working parts to a minimum. In order to fill B with dry chlorine gas, valve *f* is shut and *g* and *d* are opened. After filling, *g* and *d* are shut, *f* is opened, and petroleum is forced from D by means of a pump into A. During the compression, B is heated by a water-bath to  $50-80^{\circ}$  C., to prevent any liquid chlorine from depositing there or from being absorbed by the sulphuric acid. From vessel B the chlorine is forced by the dome E and the cooling-worm K into the pressure-pot L, where it liquefies. A liquor-gauge on E admits of observing the level of the sulphuric acid in the dome. When it has gone up as high as possible, *f* is shut, *g* and *d* are opened, and a new charge is commenced.

In the second apparatus, fig. 114, there is a U-shaped vessel, in the left leg of which a plunger *a* works in petroleum *c*, shut off by sulphuric acid, which fills the remaining space *d*, *e*, *f* of the U-shaped vessel. At the point of contact of both liquids the vessel is widened out, in order to reduce the vertical motion of the plane of contact and thus to avoid the formation of emulsions. The right leg *f* communicates with space *m* by a valve *k* and a perforation *l*, adjustable by valve *p*. Space *m* possesses the liquor-gauge *n* and the pipe *o*, through which the compressed chlorine finds its way into the cooling-worm K and the pot L. In *f* there is also a pipe *h* with valve *i*, by which on the rising of the plunger *a* dry chlorine is aspirated into *f*. *f* is heated to  $50-80^{\circ}$  by the water-bath *g*. On the rising of the plunger *a*, chlorine is drawn in through *h* and *i*, on its descending it is forced through *k*

Fig. 113.

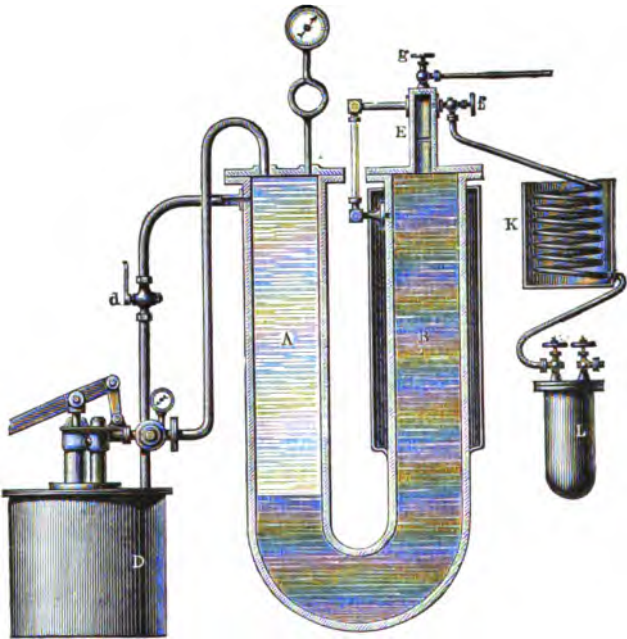
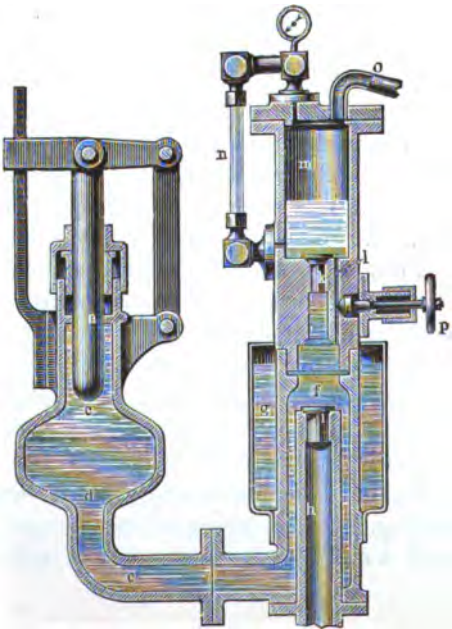


Fig. 114.





into *m*. If in this action even a small bubble of gas were to remain in *f*, this would on the rising of plunger *a* produce a large dead space, since the chlorine has to be compressed to  $\frac{1}{18}$ . For this purpose the perforation *l* is arranged; at each diminution of the pressure in *f* a little sulphuric acid from *m* enters into *f* and causes a little less chlorine to be aspirated than corresponds to the play of *a*. In consequence of this, on the descent of *a* not merely all the chlorine is forced into *m*, but also the same quantity of sulphuric acid as had previously come in through *l* into *f*. Valve *p* is regulated according to the level of the liquid in *m*.

The following metals are not acted upon by *dry* chlorine, either by itself or in contact with concentrated sulphuric acid: cast-iron, wrought-iron, steel, phosphorus bronze, brass, copper, zinc, lead. Vessels A and B are made of wrought-iron, pot L of steel, worm K of copper, valves *f* and *g* of phosphorus bronze, the packings for the flanges and valve-rods of lead, india-rubber, and asbestos.

For storing and carrying the liquid chlorine, strong iron or steel vessels are employed, which may be provided with a lining of lead, copper, or brass, to protect them against corrosion in the case of any moisture entering. The protection of the moving parts and of those in contact with air is obtained by petroleum purified with sulphuric acid, petroleum spirit or melted vaseline (comp. below).

Marx (Engl. pat. 7058, 1890) prepares liquid chlorine as follows:—Chlorine gas of sufficient strength is introduced into an outwardly cooled cylinder, into which a jet of cold water, preferably a solution of salt, is injected; solid chlorine hydrate is thus formed. This deposits on a perforated false bottom, from which the excess of water can run away. When sufficient chlorine hydrate has accumulated, the chlorine gas and water are shut off, and water, heated to 25° or 30° (or else steam, but not by preference), is passed through in a closed coil. The heat liberates from the hydrate pure chlorine, which is again cooled in an outwardly cooled cylinder; here the steam carried away condenses as chlorine hydrate. The dry chlorine is now condensed to a liquid by pressure, and further cooling in the iron stock-bottles themselves, without any pumping. The patent also shows an arrangement for transferring the liquid from the iron stock-bottles into vessels made of a material of greater chemical resistance, consisting of a metallic shell with glass lining, the latter being firmly

pressed against the former by means of a plastic layer of boiled linseed oil, gutta-percha, india-rubber, or the like.

Cutten (Engl. pat. 89, 1892) thoroughly dries the chlorine, first by outward water-cooling, then by calcium chloride, and at last by sulphuric acid; it is then compressed by means of a pump in steel vessels to four atmospheres; the heat generated thereby is carried away by cold-water coils lying in the liquid chlorine. Uncondensed air, &c., escapes through a safety-valve.

The German works send out the chlorine in iron bottles (called "Bomben" = shells), tested for a pressure of 50 atmospheres, and containing 60 kilogrammes chlorine. They are 4 ft. 4 in. long,  $8\frac{1}{2}$  in. wide, and made of 0.4 inch plate, with two valves, from which the chlorine can be taken, either as a gas or in the liquid form. Hasenclever (Chem. Ind. 1893, p. 373) gives a drawing and description of these; they are similar to those shown Vol. I. p. 295 in connection with liquid sulphur dioxide, but different in some details.

## CHAPTER XVII.

## THE UTILIZATION OF STILL-LIQUOR.

THE "still-liquor" produced in the ordinary chlorine-manufacturing process contains chiefly manganous chloride, together with ferric chloride and the chlorides of any other metals occurring in the manganese ore, and also a considerable quantity of free hydrochloric acid and free chlorine. The liquor at Dieuze had, according to Hofmann, the following average composition:—

Manganous chloride.....	22·00
Ferric                   ,,       .....	5·50
Barium                   ,,       .....	1·06
Free chlorine.....	0·09
Hydrochloric acid.....	6·80
Water       .....	64·55
	<hr/>
	100·00

Black (Transactions of the Tyne Social Chemical Society) gives the following analysis of still-liquor obtained with native manganese:—

HCl .....	6·6220 = 6·622 per cent. HCl.		
Al <sub>2</sub> Cl <sub>3</sub> .....	0·6200 = 0·500	,,	,,
MnCl <sub>2</sub> .....	10·5700 = 6·120	,,	,,
Fe <sub>2</sub> Cl <sub>6</sub> .....	0·4551 = 0·310	,,	,,
H <sub>2</sub> O .....	81·7329		
	<hr/>		
	100·0000	13·552	

Hence, of 13·552 HCl found, only 6·120, *i. e.* 45 per cent., was combined with manganese. Now, even if all the Mn had been originally present as MnO<sub>2</sub>, only an equal quantity (6·120) of

HCl had escaped as chlorine ; so that the total HCl originally employed amounted to 19·672. Accordingly the HCl usefully employed was only 62·2, that combined with iron and aluminium 4·1, and that found free 33·6 per cent. of the whole.

The acid still-liquor has always been a source of great embarrassment to the producers of chlorine. On running-off the stills it causes a fearfully suffocating smell of chlorine, which in the case of large quantities is perceptible at distances of half a mile and upwards ; in the watercourses into which it is discharged it destroys all fish, it damages the foundations of buildings, quays, and bridges, &c. Moreover all manganese contained in it is lost. Hence very many proposals have been made for utilizing the still-liquors, partly only with a view to employing the free acid, partly for making the manganese available in some shape, and partly for regenerating  $\text{MnO}_2$  from them.

The latter are of much greater importance than the former. Before the "recovery of manganese" from the still-liquor in a state suitable for the renewed manufacture of chlorine had come to a successful issue, the rapid extension of that manufacture had caused a sharp rise of the price of manganese ore, which, during the years 1871 to 1873, amounted to twice the price of former years. But at that period a great recoil took place, partly in consequence of the complete success of Weldon's manganese recovery process, which reduced the consumption of manganese ore to a small fraction of that which had existed previously, partly through the Deacon process, in which no manganese at all is used, and partly through the discovery of several important new occurrences of manganese ore (p. 269).

#### UTILIZATION OF STILL-LIQUOR WITHOUT RECOVERY OF DIOXIDE.

Laming (Engl. pat. 11944, 1847) proposed to manufacture man- ganous carbonate from the chloride by means of chalk or gas- liquor, and to employ this for *purifying coal-gas* from sulphuretted hydrogen. Later on (No. 1480, 1859) he proposed to make the  $\text{MnCO}_3$ , or else  $\text{Mn}(\text{OH})_2$  or  $\text{MnS}$ , more active by mixing with sawdust and oxidizing in the air. It is true that manganese in this form is a very good absorbent of  $\text{H}_2\text{S}$ , but it has been abandoned in the gas-works for ferric hydroxide, especially in the shape of bog-iron ore. For other cases where  $\text{H}_2\text{S}$  has to be

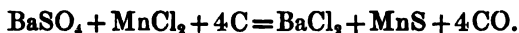
absorbed, it has been proposed by myself (Engl. pat. 1108, 1866) and several times by Weldon.

A similar proposal is that of Dales (Engl. pat. 2157, 1859), according to which the still-liquor is to serve for deodorizing faecal matters; this has been proposed several times over.

Gossage (Engl. pat. 2630, 1856) employs, apart from other carbonates, also manganous carbonate, made from still-liquor, for decomposing *sodium sulphide* in the alkali-manufacture.

Still-liquor has been proposed for use in the *recovery of sulphur from Leblanc waste* by several inventors, partly in order to precipitate MnS, partly only in order to utilize the free acid contained therein; for instance, by Townsend and Walker, Schaffner, P. W. Hofmann, Mond (Vol. II. pp. 828, 829, 844).

The formation of MnS is also the important point in the manufacture of *barium chloride* from the natural sulphate of baryta by means of still-liquor. This process seems to have been invented by Kuhlmann (Compt. Rend. xlvii. p. 164); the patent taken by Clark (No. 2650, 1856), as a communication from abroad, probably belongs to Kuhlmann. The same process forms the subject of a provisional protection obtained by Seitz (No. 1898, 1860). The free acid is saturated by barium or calcium carbonate, the liquid run into a furnace charged with a mixture of ground sulphate of baryta and coals, and the mixture heated for several hours in a reverberatory furnace, where barium chloride and manganese sulphide remain behind and carbon monoxide burns away:



The two former are separated by lixiviation, and the barium chloride obtained by evaporation and crystallization. Kuhlmann recommends the following proportions:—100 parts of ground sulphate of baryta, 40 coal, 170 saturated solution of manganous chloride, 13 chalk or lime; or 320–400 still-liquor, 100 barium sulphate, 30 to 35 coal (no lime). The MnS remaining behind on dissolving cannot be utilized; it yields too poor a gas for sulphuric-acid chambers when burnt. This process was carried out for a considerable time, but abandoned, as it was found that manganous chloride can be replaced by calcium chloride.

A series of proposals refers to the application of still-liquor, or of manganese compounds prepared therefrom, in the *manufacture of iron and steel*: e. g. Hunt (Engl. pat. 81, 1855); Henderson

(No. 3438, 1862) ; Schaffner (Wagner's Jahresb. 1868, p. 225). Since great masses of manganese ore are brought into the market which contain but little peroxide, but are otherwise perfectly suitable for the above purpose, those proposals have become quite useless.

In the *glass-manufacture* manganese oxides precipitated by lime from still-liquor have been employed instead of the rich manganese ores otherwise used in that manufacture (Wagner's Jahresb. 1873, p. 282).

As a *colouring-matter* the brown colour produced upon the fibre itself by means of manganous chloride has been employed for a long time, under the name of "bistre." For this purpose crystallized manganous chloride has been manufactured.

Crockford (patent, July 25, 1863) proposes to employ the precipitate produced in still-liquors by lime as a pigment. Leykauf (Dingl. Journ. exc. p. 70) also makes a colour from still-liquor by fusing the dried product with phosphoric acid, boiling with ammonia, filtering, drying down the filtrate, fusing again, and exhausting with boiling water ; the colouring matter which he called "Nuremberg purple" remained behind.

*Pure manganous chloride* can be prepared for these purposes from still-liquor in the following manner :—After neutralizing the free acid, Muspratt and Gerland (Engl. patents, 2922, 1856, and 1589, 1857) precipitate the iron by calcium carbonate, remove it by filtering, then precipitate the copper by  $H_2S$ , and, after the removal of the  $CuS$  by calcium sulphide or soda waste, the nickel, cobalt, and a portion of the manganese as sulphides, the  $MnS$  is extracted from the mixture by weak acid. Copper, cobalt, and nickel, which may also be precipitated together by calcium sulphide, are utilized in the ordinary manner ; and the manganous chloride remaining in the mother liquor may be employed for recovering  $MnO_2$ .

The *free acid* of still-liquor has been proposed for a great many uses :—*e. g.*, by Kuhlmann for absorbing the ammonia formed in the dry distillation of bones (patent, No. 1620, 1855) ; by T. A. Cook for purifying manganese itself from iron, earthy carbonates, &c. (patent, No. 2570, 1856) ; for making  $CO_2$  from carbonates many times ; for extracting copper-ores by Haefely and by Deane (prov. prot. No. 753, 1866 ; Chem. News, xiv. p. 287).

## THE RECOVERY OF MANGANESE PEROXIDE FROM STILL-LIQUOR.

This is of course by far the most important mode of utilizing still-liquor; and it has been aimed at by a great number of proposals, which will be briefly enumerated here, reserving only Weldon's, which has been entirely successful, for detailed description.

*By the Action of Atmospheric Air on Manganese Protoxide, precipitated by Lime.*—This process, which has finally turned out the only available one, was, accidentally, also the first proposed for recovering  $\text{MnO}_2$ ; Gossage prescribes (in a patent, No. 7416, 1837) the precipitation of still-liquor with lime, running off the  $\text{CaCl}_2$  liquor, and bringing the residue into violent contact with air. The next step was made by Binks and Macqueen (patent No. 1240, 1860): they passed air, either cold or, preferably, heated to  $200^\circ$  or  $300^\circ$  C. and upwards, through water in which manganese oxide precipitated by lime was suspended. The peroxide formed in this way was to be agglomerated into lumps by pressing in the damp state or moistening with a hot saturated solution of  $\text{MnCl}_2$ , and drying. Weldon's first patent dates from July 26, No. 1948, 1866; the further steps of his invention will be mentioned further on.

Binks had already, in 1839 (No. 7963), patented the precipitation of  $\text{MnO}$  by alkalies and heating the precipitation in the air; but he lays most stress on the subsequent treatment with nitrate of soda. Walters patented (No. 9676, 1843) heating manganese sulphate (obtained as residue on treating manganese ore with equivalent quantities of sulphuric and hydrochloric acids), admitting "a small quantity" of air; "manganese" is obtained; and the  $\text{SO}_2$  evolved may be converted into sulphuric acid. Glover (prov. prot. No. 1417, 1853) purposes to regenerate "black oxide of manganese" by heating manganous chloride in contact with air. Balmain (patent No. 723, 1855) precipitates the still-liquor by ammoniacal gas-liquor, obtains from the solution ammonium chloride, and from the precipitate, filtered on sand and heated to a red heat, manganese peroxide. It is advisable to mix lime with the wet sediment before igniting it. Haefely (No. 1505, 1858) patented exactly the same thing. Elliott (patent, No. 2392, 1856) proposes to decompose by heat the  $\text{MnCl}_2$ , purified from iron, into free  $\text{HCl}$  and a mixture of

MnO and  $\text{MnO}_2$ , from which the former is dissolved out by weak acid. Pattinson (prov. prot. No. 2475, 1856) precipitates MnO by lime, and exposes it to a carefully regulated heat below the melting-point of tin, in order to obtain  $\text{MnO}_2$ . Essentially the same thing was again patented by Hunter (No. 1354, 1860). As No. 2066, 1866, Clark (for Cotelte) patented the heating of acid manganese-liquor in a reverberatory furnace; in the residue  $\text{MnO}_2$  is said to remain. If HCl is admitted, the same  $\text{MnO}_2$  is to decompose it continuously into chlorine and water [of course with the assistance of atmospheric oxygen].

Claus (No. 1054, 1867) patents the same process; he absorbs the weak chlorine by a shower of water holding hydrated lime or magnesia in suspension, and treats the hypochlorites formed with hydrochloric acid, to obtain strong chlorine.

Gorgeu (Compt. Rend. vol. lxxxviii. p. 769) states that by heating manganous nitrate and keeping it for a long time at a temperature of  $155\text{--}162^\circ$  a compound having the same composition as the mineral polianite is formed.

The process of Jezler (Dingl. Journ. ccxv. p. 446) is only a modification of Weldon's process: it likewise aims at the manufacture of a calcium dimanganite,  $2\text{MnO}, \text{CaO}$ , but as a dry powder. Pure  $\text{MnCl}_2$  solution is to be precipitated with thick cream of lime; one half or a little more of the quantity required for precipitation is to be added, the precipitation separated from the liquor and spread out in the air. After drying it a little, it is exposed to a temperature of from  $30^\circ$  to  $40^\circ$  C. for some time, agitating it, and replacing the water evaporating. When the mass has become black by absorbing oxygen, it is deprived of most of the  $\text{CaCl}_2$  by washing, and the oxidation finished by raising it to a higher temperature [how much?]; at the end the  $\text{CaCl}_2$  can be completely washed out. If the first oxidation takes place when the mass is still liquid, a moment arrives when the voluminous and flaky sediment becomes dense; and then the  $\text{CaCl}_2$  can be easily removed. But the lime ought not to be removed by washing too soon; for only the proper proportion between Mn and Ca yields a high-strength dimanganite. The product is sometimes brown, sometimes black; it equals the best native manganese ore as regards the consumption of hydrochloric acid, and gives off most chlorine even in the cold; and the still requires only moderate heating towards the end. Powdery recovered manganese dioxide can be formed into lumps



which are rendered more solid after drying, by adding a small percentage of the semi-oxidized mass which had not been heated and contains calcium chloride. [This process has never been applied on the large scale.]

A proposal patented by Valentin (No. 1837, 1870) has but very little prospect of realization. Potassium ferricyanide is to serve as carrier of oxygen to precipitated  $\text{MnO}$  in the form of mud; the ferrocyanide formed is to be reoxidized into ferricyanide by a current of air, and in this way a continuous action is exercised similar to that of nitrous acid in the manufacture of sulphuric acid. Less than 0.5 per cent. ferricyanide upon the weight of the manganese is to suffice for regenerating the latter; but the high price of that compound would make this loss quite sensible; and it could not be left in the manganese mud, because in that case very poisonous cyanogen compounds would be formed along with chlorine. Washing out the ferricyanide would entail the filtering and treatment of a very large bulk of mud, and could not possibly pay the expense.

De Sussex and Arrott (patent, No. 10296, 1844) precipitate  $\text{MnO}$  from the liquors, and ignite it in a reverberatory furnace with potash or soda in the state of hydrate or carbonate; the fused mass is dissolved, and from the liquor  $\text{MnO}_2$  precipitated by the  $\text{CO}_2$  of the air, or by  $\text{CO}_2$  prepared for the purpose.

*Treating the lower Oxides of Manganese with weak Acid* for washing out  $\text{MnO}$ , whilst the  $\text{MnO}_2$  remains behind.—This is one of the many proposals, mostly somewhat obscure, in Binks's patent of 1839. De Sussex and Arrott, according to their patent just mentioned, dry down the still-liquor, heat the residue with lime or magnesia, and treat the oxide thus obtained with weak hydrochloric acid to dissolve  $\text{MnO}$ ; they also do this with natural low-strength manganese ore. Elliott and Pattinson obtained provisional protection far exactly the same thing (No. 992, 1856).

*Heating Manganese Chloride with Ferric Oxide.*—Macfarlane (Engl. pat. 9234, 1884) mixes dry  $\text{MnCl}_2$  with from one to four times its weight of ferric oxide, and heats the mixture to  $400^\circ \text{C}$ . in a current of air dried by calcium chloride; dilute chlorine escapes, and a mixture of ferric oxide with  $\text{Mn}_2\text{O}_4$  and  $\text{MnO}_2$  remains behind. On treating this mixture with hydrochloric acid, practically only the manganese oxides are acted upon, with evolution of chlorine, and the ferric oxide remains almost unchanged.

The mixture is again brought to dryness, and the residue is used over again as at first.

*Igniting with Nitrate of Soda.*—Binks (No. 7963, 1839) heats dried-down still-liquor, or lower oxides of manganese prepared in any way, with nitrate of soda to a dark red heat in a retort; lime or chalk may also be added. His mixture consists of 1 part nitrate of soda, 2 dry "sulphate residue" (*i. e.* residue from evolving chlorine by sulphuric acid, common salt, and manganese), and 3 parts of the lower manganese oxides or carbonates, obtained by his process—or else 1 part nitrate, 8 parts dry "sulphate residue," and 3 parts calcium hydrate or carbonate. The residue on being washed furnishes  $\text{MnO}_2$ ; the  $\text{NO}$  escaping is to be brought into contact with a further quantity of the lower oxides or carbonates of magnesia in a moist state. The latter part of this proposal is repeated in the patent of De Sussex and Arrott (1844). Gatty patented (No. 2230, 1857) essentially the same thing as Binks.  $\text{MnCl}_2$  or  $\text{MnSO}_4$  is to be mixed with its equivalent of sodium nitrate, the mixture dried and heated to a dark red heat in an iron retort. "Black oxide of manganese" remains behind, along with sodium sulphate or chloride, which is separated by lixiviation; the escaping nitrous gases are to be utilized for the manufacture of sulphuric acid.

This process was again taken up by Kuhlmann (Compt. Rend. *lv.* p. 247), who, however, converts the nitre-gas by air and water into nitric acid. In this way, from 100  $\text{NaNO}_3$ , 125 or 126 nitric acid of sp. gr. 1.320 are said to be obtained, *i. e.* not much less than in the ordinary manufacture of nitric acid. According to Péan de St. Gilles (Rép. Chim. appl. 1862, p. 338) the decomposition commences at  $220^\circ \text{C.}$ , and lasts for 8 or 10 hours. The residue is not  $\text{MnO}_2$ , but an oxychloride of the formula  $3\text{Mn}_2\text{O}_3, \text{MnCl}_2$ , which is very unsuitable for chlorine-making. A further application of the nitrous vapours proposed by Kuhlmann was, passing them over  $\text{Mn}(\text{OH})_2$ , which is thereby converted into  $\text{MnO}_2$ . Kuhlmann asserts (Beilstein, Chem. Grossindustrie, 1873, p. 42) that in this case manganous nitrate is re-formed, which on being heated to  $200^\circ$  leaves  $\text{MnO}_2$  behind and gives off all the nitrogen as available nitrous vapours, not as  $\text{NO}$  or  $\text{N}$ ; thus the atmospheric oxygen might be transferred upon  $\text{MnO}$  *ad infinitum*. Kuhlmann patented this process for England, No. 847, 1873. He precipitates the still-liquor with only one equivalent of lime, and consequently

asserts that he gets an 88-per-cent. peroxide [?], while he states that Weldon's process only yields 70-per-cent. peroxide. Another proposal of the patent is, draining the  $\text{Mn}(\text{OH})_2$  on coarse matting and employing it for Bessemer-steel making. The latter proposal seems to betray small confidence in the former. To this class belong also some proposals for converting manganous nitrate into  $\text{MnO}_2$  by heating, which will be described in the last chapter of this section, *e. g.* that of Schloesing.

*Heating of Manganese Carbonate.*—This process was patented by Dunlop on May 31st and Nov. 22nd, 1855 (Nos. 1243 & 2637), and was for many years practised at St. Rollox. The same process was also patented by Gossage on August 30, 1855 (No. 1963), but too late. An improvement by Clemm (Dingl. Journ. clxxiii. p. 128), viz., employing magnesium carbonate instead of calcium carbonate in this process, and regenerating  $\text{HCl}$  by heating the magnesium chloride, has not been practically realized. Neither has this been the case with the proposal of Binks and Macqueen (patent No. 1240, 1860) for passing hot air through  $\text{MgCO}_3$  suspended in water. It appears that the reaction upon which Dunlop's patent and other similar proposals are founded was discovered by Forchhammer: it has been especially investigated by Reissig for a large number of temperatures and different durations of the heating process (Ann. Chem. Pharm. ciii. p. 27). He found a temperature of  $300^\circ$  and three hours' action most favourable: the product then contained 73 per cent.  $\text{MnO}_2$ , and corresponded to the formula  $2\text{MnO}_2, \text{MnO}$ . [This would square exactly with Weldon's theory, that in his recovery-process the reaction stops at the formation of an "acid manganite."]

Dunlop's process is as follows:—The acid still-liquor is first neutralized with ground chalk in open agitating-apparatus; the iron is also precipitated as hydroxide, but no manganese. The neutral liquor is pumped into very large, horizontal, cylindrical wrought-iron boilers, about 10 feet in diameter and 80 feet long, fitted with a horizontal agitating-shaft. Here the liquor is mixed with the requisite quantity of ground chalk (excess of which is to be carefully avoided); the boiler is tightly closed, and by blowing in steam the pressure raised to 2 or  $2\frac{1}{2}$  atmospheres. By means of the pressure, the heat, and the agitation, complete decomposition is effected in 24 hours, producing a solution of  $\text{CaCl}_2$  and a white precipitate of  $\text{MnCO}_3$ ; while under ordinary circumstances this

reaction does not take place. The contents of the boiler are forced by steam-pressure into settling-tanks; the  $\text{CaCl}_2$  liquor is run off, the precipitate well washed, pressed, and partially dried on iron plates. It is now put into shallow iron bogies running on wheels, and introduced into a peculiar kind of oven divided by arches into four tiers one above the other, each of which holds twelve of those bogies; inside these are rails, upon which the bogies run with ease. The oven is heated from without, so that its temperature reaches  $315^\circ \text{C}$ .; it is hottest at the bottom. A current of air enters at the lowest tier and passes through all four. Each fresh bogie is introduced at one end of the top tier, where it meets the coolest temperature and an atmosphere rather poor in oxygen; the bogies are gradually moved onwards, that at the end of each tier getting into the next lower tier; and they thus constantly meet a warmer air, richer in oxygen, which assists the conversion of the moist manganese carbonate into peroxide. The moisture must be renewed by frequent squirting of water. As a fresh bogie is put in once an hour, and the others must all be moved onwards accordingly, each of them remains in the oven for 24 hours. When they come out, their contents test 72 per cent.  $\text{MnO}_2$ ; the remaining 28 per cent. are lower oxides of manganese and about 2 per cent. calcium carbonate. The thick paste is worked up for chlorine by  $\text{HCl}$  as usual, and is much more easily dissolved than native manganese. The plant required for this process is extremely costly, and has never been put up for the whole of the still-liquor even at St. Rollox. Outside of those works the process seems to have been tried only at Thann (Wagner's *Jahresb.* 1858, p. 122; Hoffmann, Report by the Juries, 1862, p. 37); but it was there given up after a short time, as the expense of fuel made it unremunerative.

Dunlop's recovery-process has not been introduced by Messrs. Tennant at their Hebburn works, erected about the year 1870; it has also long ago been abandoned at St. Rollox for the manufacture of chlorine, but it seems to be still employed there in manufacturing pure manganic oxides for special purposes.

Recently at the same works (St. Rollox) the recovery of  $\text{MnO}_2$  by the formation of  $\text{MnCO}_3$  has been tried in another way. Campbell and Boyd (pat. 10187, 1888) heat manganous chloride with sulphuric acid and some more manganese ore, whereby nearly all the chlorine is obtained in the free state, the manganese being transformed into sulphate. This is dissolved in water and is

treated with ammonium carbonate (probably in the shape of crude gas-liquor), to obtain  $\text{MnCO}_3$ , which is transformed into  $\text{MnO}_2$  by Dunlop's process; the ammonium sulphate formed in this way is sold as such. [This means that in any case the process would be only capable of limited application.] Patent No. 18056, 1888, modifies the first part of the invention by passing gaseous  $\text{HCl}$  into a solution of  $\text{MnSO}_4$ , to which so much  $\text{MnO}_2$  has been added that by the aid of more sulphuric acid all the chlorine of the  $\text{HCl}$  is liberated. [Campbell and Boyd's recent patents are enumerated in the last chapter of this section.]

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#### THE OLD WELDON CHLORINE-PROCESS.

All the numerous proposals for recovering the manganese have resulted in failure, with only two exceptions, viz. the processes of Dunlop and of Weldon. In all other cases either the recovery of  $\text{MnO}_2$  costs more than fresh manganese ore, or the chlorine obtained is too dilute, or for some other reason the process does not pay. Of the two processes just mentioned we need not recur to Dunlop's, although in 1880 still 5000 tons of bleaching-powder per annum were made by it, because, for the reasons already given, this process has not extended beyond the St.-Rollox works, where it originated; the same firm, at their new works at Hebburn-on-Tyne, introduced the Weldon process, and not the Dunlop—which makes further comment unnecessary (p. 322).

The recovery of  $\text{MnO}_2$  by the action of a current of air upon  $\text{Mn(OH)}_2$  precipitated by lime has been repeatedly proposed (p. 317). Nearest to the mark came the process of Binks and Macqueen (1860); but they also did not succeed. It is the undoubted merit of Mr. Walter Weldon to have discovered the right way. He also, as shown by his first patent of 1866, was not at first on the right track, but found it by persevering experiments when he had an opportunity of working out the process at the works of Messrs. Gamble & Co. at St. Helens, where, according to his own statements, he met with most efficient assistance by the technical skill of the manager, Mr. Bramwell.

Weldon's process is founded on the fact that freshly precipitated manganous hydroxide, suspended in a solution of calcium chloride, is, *in the presence of an excess of lime*, easily converted

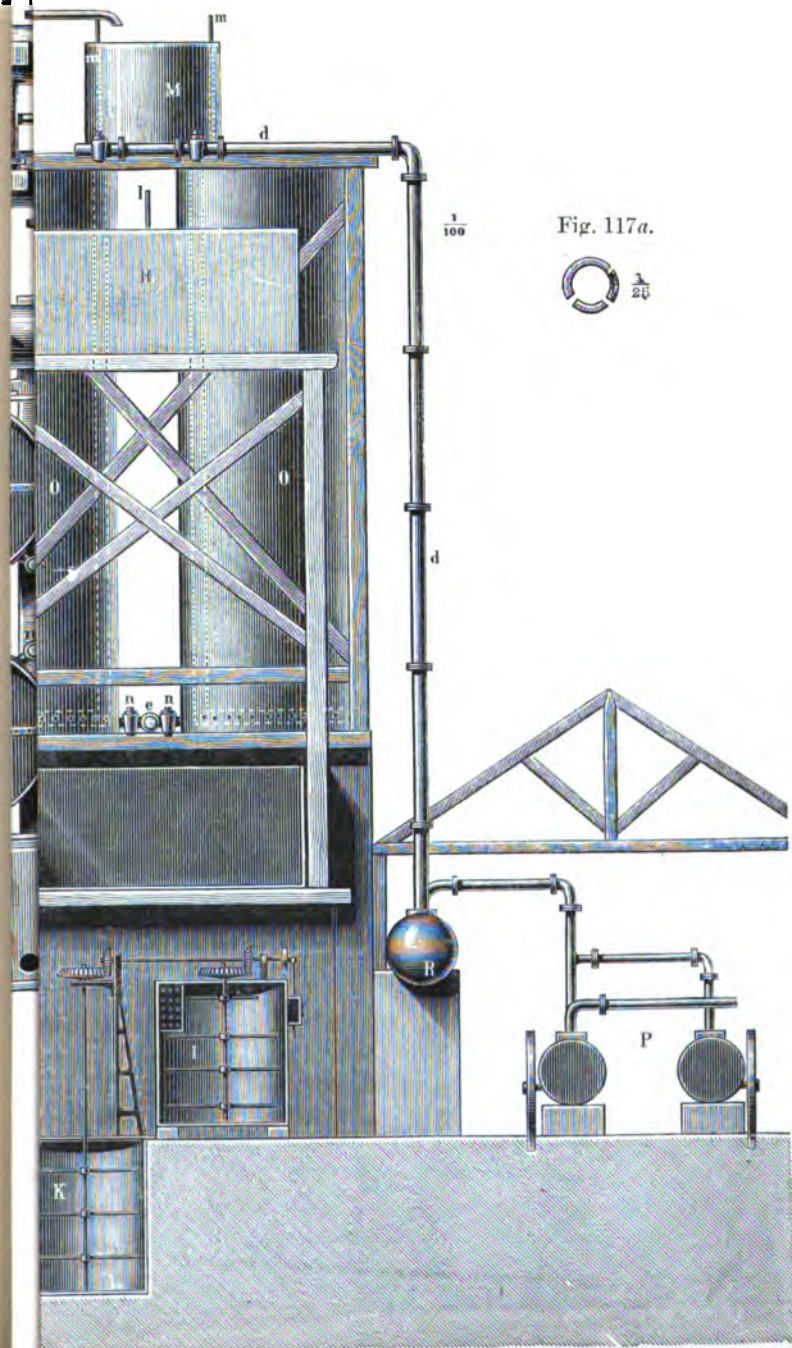
into peroxide by a current of air forced through the liquid. It is this *excess* of lime that has made the process successful. It had long been known that  $\text{Mn}(\text{OH})_2$  can be to a certain extent oxidized as it is precipitated from still-liquors by its equivalent of lime; but this oxidation remains so incomplete as to be useless in practice. Weldon found that manganous oxide treated in the wet way with air could at most be half-converted into peroxide, so that  $\text{Mn}_2\text{O}_3$  is formed; but when a certain quantity of lime is added, the  $\text{MnO}$  under favourable circumstances can be completely converted into  $\text{MnO}_2$ , and that in less than one tenth of the time which is necessary for forming  $\text{Mn}_2\text{O}_3$  in the absence of lime. This was the key to the splendid success which his process has had. But it should not be overlooked that Weldon has also worked out the technical details both of the plant and the process with great perseverance and care, so that everywhere the apparatus could be erected and started from his instruction without any difficulty. There is all the difference in the world between the crude and economically useless proposals of Binks and Macqueen, and the Weldon process, which now forms an integral part of the operations of most larger alkali-works, both in England and on the Continent. This process is now almost more easily and safely carried out than any of the long-known operations in alkali-works. Weldon's merit has been fully recognized abroad by the bestowal upon him of the grand Lavoisier medal, and of a "Grand Prix" at the Paris exhibition of 1878. He must be said to have largely benefited chemical industry in general, and, by cheapening bleaching-compounds, also the bleach-trade and paper-making and the carrying-out of disinfection—that is, all mankind.

Weldon's manganese-recovery process is inseparably connected with his process of generating chlorine from the recovered peroxide. It is, on the whole, carried out everywhere according to the same principles and in very similar apparatus. The following description refers to an apparatus with which 6 tons of bleaching-powder daily can be made by working single shifts, or 12 tons by day-and-night work; but in the latter case the stills should be larger, as they are afterwards represented in special drawings. Fig. 115 is a side elevation of the apparatus, fig. 116 a plan on the line A B of fig. 115, fig. 117 a section on the line C D of fig. 116.

E E are the mud-stills, which are here taken as 7 feet square and 10 feet high; their construction will be described in detail

Fig. 117.

[To face p. 324.







afterwards. T is an ordinary still, which serves for dissolving native manganese ore, to make up for the loss in recovery, and which is so fixed that its waste liquor can be discharged directly into one of the mud-stills E. F is the neutralizing-well, which receives the manganese liquor from E; this also will be described below. G is a pump, made of cast iron, with bronze piston, valves, &c.; it conveys the neutral manganese liquor, free from iron, by the pipe *a* to the wrought-iron settlers H H. They are worked by a special engine as double-acting force-pumps with a 6-inch barrel, and are built very substantially, so as to seldom require repair. Their valves must be easily accessible. Their suction- and delivery-pipes are 4 or 5 inches wide; the suction-pipe, so far as it dips into the manganese liquor contained in the neutralizing-well, is sometimes made to turn on a swivel; it is then ordinarily protected from contact with the acid liquor, and need only be let down when the pump is to work. Failing this arrangement, there should be a few suction-pipes in reserve, as they are quickly corroded. There is a running-off cock attached to the delivery-pipe, by which the liquor standing in it is run back into the well. In order to make the pressure more uniform, and, as it were, to serve as an air-vessel, the upper end of the delivery-pipe *a* is continued 6 feet above the side branch conveying the liquor to the settlers.

*The chloride-of-manganese settlers* H H are made of  $\frac{3}{8}$ -inch boiler-plate, or of cast-iron flanged plates bolted together, with the usual strengthening stays. Wooden tanks caulked, or lined with lead, are very disadvantageous; the extra cost of the iron vessels is very quickly made up by saving the expense of the repairs and the long stoppages connected with the other kind of vessels. Well neutralized manganese liquor does not act at all upon the iron. There must be at least two settlers, in one of which the liquor is left at rest while the other is being pumped into. Each of them is provided with a side discharge-pipe and sluice-valve *b* not far above the bottom: this is continued inside into a swivel pipe like that shown in figs. 261 and 262, in Vol. II. p. 694, or sometimes into a 4-inch india-rubber pipe, so that the liquor can be drawn off clear from the mud. The discharge-pipes unite outside in an iron pipe, which divides again into two branches, one for each oxidizer O O, provided with a sluice-valve each. These branch pipes enter the oxidizers at about two-thirds

of their height. The manganese liquor is pumped alternately into one or the other settler. This is mostly done by separate valves for each; but a wooden or iron box *k*, with a plug-hole for each compartment, answers the same purpose. Each settler also has a large conical bottom-valve, worked by the handle *l*; by these the mud is removed from time to time. Below they discharge into large wooden or iron shoots (not shown), which convey the mud to a suitable place for further treatment.

The settlers H H may be each about  $11 \times 12 \times 6\frac{1}{2}$  feet, holding, when full, about 50 tons—making, along with their own weight, together about 104 tons. Consequently they must be very firmly mounted, especially as this has to be done at a great height above the ground. This is always effected by a wooden framework of 12- to 14-inch square beams, resting upon the same foundation as the mud-settlers S S. This framework is represented in the drawing without the necessary staircases, gangways, &c.

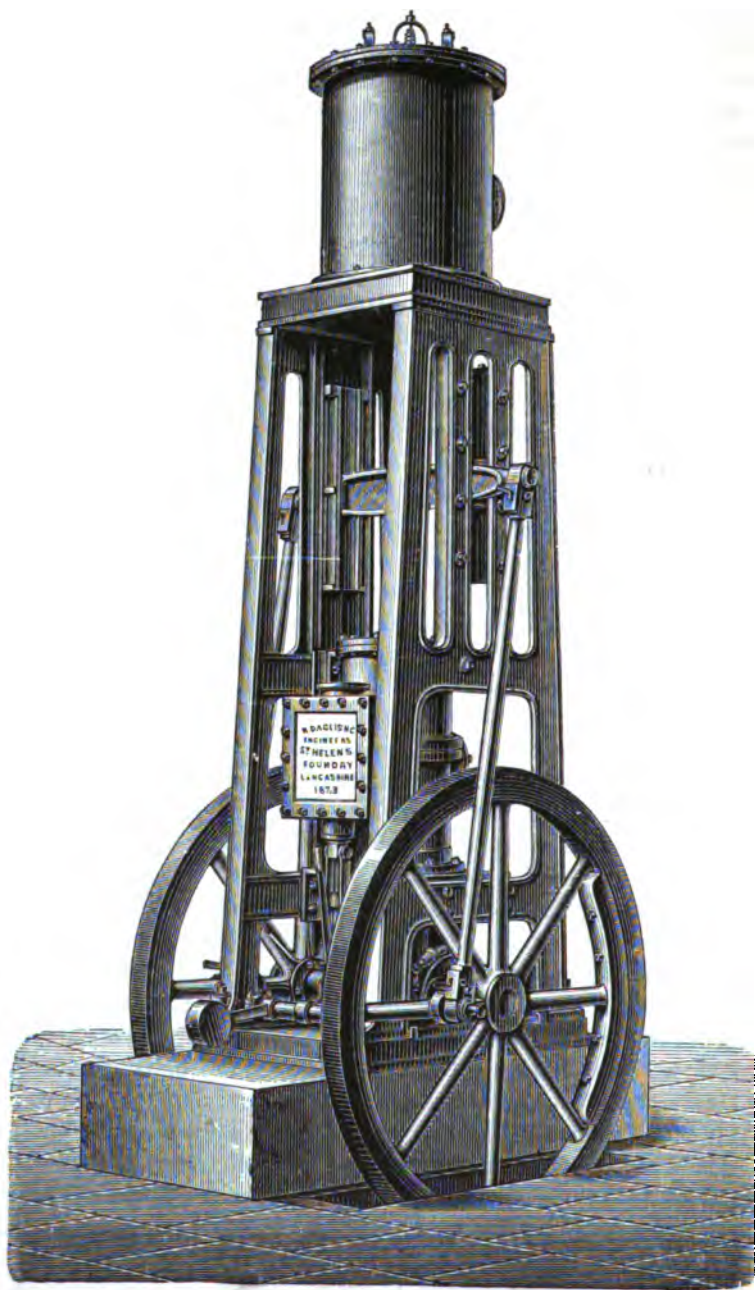
In the *oxidizers* O O the recovery proper takes place. They are wrought-iron cylinders,  $\frac{3}{8}$  inch thick (the upper third, which never contains liquid, but only froth, may be  $\frac{1}{4}$  inch), open at the top, and with a flat bottom. They stand on a strong foundation, mostly of brickwork, upon which a wooden framework is erected for keeping the oxidizers in their places and preventing them from shifting, notwithstanding the strong shaking on forcing the air through. The oxidizers are filled with settled manganese liquor by the pipes *b b*, and are fed with milk of lime either directly by the pump L and the delivery-pipe *c*, or preferably from the iron tank M, into which the milk of lime is pumped first, and which discharges into either oxidizer by a separate valve *m m*; these are in the drawing shown only as plug valves; but they must actually be constructed in such a way that they can be regulated as well from the foot of the oxidizer. The upper lime-tank M must also be provided with an agitator; and since the application of machinery at that height occasions difficulties and expense for shafting, it seems advisable to fix a Korting's injector there and agitate by a current of air. The unavoidable dilution by steam can do little harm during the short time this agitation goes on. Or else a small branch of the large blowing-pipe is put in to stir up the milk of lime. When this vessel M is not present, the oxidizers remain quite open; and in any case only a small portion is covered by bearers &c. The 7-inch pipe *d* conveys compressed air into

the oxidizers; it comes from the air-vessel R, and sends a branch with valve to each oxidizer. This pipe, in spite of the greater expense and the loss by friction, must be carried to the top of the oxidizers and then descend to the bottom inside; otherwise the connecting flanges could not be kept right, owing to the shaking during the blowing. The same thing holds good of the milk-of-lime pipe and the steam-pipe; but as a fixed connection cannot be dispensed with in the case of the manganese-liquor pipe *b*, I found it suitable to interpose in this pipe, between the oxidizers and settlers, an equally wide (4-inch) india-rubber pipe, which entirely prevents the movements in O O being felt in the settlers H H. The air-pipe *d* descends to the bottom of O, and there branches off in the form of a cross, or in some other way, so that the blast is divided into many jets. The branches are closed at the end, and are perforated with a number of 1-inch holes slanting downwards (fig. 117, *a*); thus the mud does not penetrate into them so easily. Each oxidizer has also a 2-inch steam-pipe (not shown), passing over its top down to the bottom and branching off there; the steam-valve is placed outside in a convenient position for the attendant, near a  $\frac{1}{2}$ -inch test-cock, 5 feet above the bottom. These are generally in or close to a small lavatory (testing-cabin) built against the oxidizer, from which also the valves for the milk of lime are accessible, and which is connected with the engine-room for the blowing-engine by an open communication, or at least by a speaking-tube. The discharge-pipes *n n* (6 inches wide) start from the bottom of the oxidizers, each provided with a sluice-valve, and continue into a common pipe *c*, which sends out a branch with 4-inch valves over each mud settler.

The *manganese mud-settlers* S S are built just like the liquor-settlers H H and of the same size; but there must be at least 3, better 4 of them, provided. Each is fitted with a 2-inch swivel pipe *i* for running off the calcium-chloride liquor; these communicate on the outside with a common pipe or, better, an open spout, conveying the liquor to a catch-well. At the bottom there is a 4-inch pipe *f* with sluice-valve, joined to the main pipe *g*, from which each of the stills E is fed by a pipe and sluice-valve *h*.

For producing the current of air the following arrangements are made:—Two steam-boilers N N, of about 6 feet diameter and 30 feet long, supply the steam for the blowing-engine P and all

Fig. 118.



other steam required in the process (for the oxidizers, milk-of-lime tanks, chlorine-stills, pumps, and agitators). In case of need, *e. g.* during cleansing or repairs, one boiler may work by itself; but then all the operations cannot be performed at one time. The blowing-engine P in this case is sketched as a horizontal twin-engine, with two steam-cylinders of 18 inches diameter, air-cylinders of 2 feet 2 inches diameter, and 2 feet stroke; one of the cylinders may work by itself in case of repairs, but not so well. All the valves of the air-cylinders are of india-rubber. This is the kind of blowing-engine built by Messrs. Neill and Son of Bold; others prefer the vertical engine, fig. 118, built by Messrs. R. Daglish and Co., of St. Helens, with a 20-inch steam-cylinder, 2-ft. 3-inch air-cylinder, 3-feet stroke, and an 8-foot fly-wheel. The blast passes from the engine first into a regulator or air-vessel R (fig. 116) of any shape, and from this by the 7-inch pipe *d* to the oxidizers. To the air-vessels a pressure-gauge and a pipe for running off the water are fixed; the latter comes from the air-cylinders, which are lubricated by a continuous small jet of water. The dry compressors, built by Messrs. Burkhardt & Co. of Basel, work without water, and are said to be more economical on that account and in other respects.

The blowing-engines will have to make from 40 to 60 strokes per minute, according to the amount of work to be done. For each ton of bleaching-powder to be made, about 300,000 cubic feet of air or one hour's work of 40- to 45-horse power may be taken as necessary. The exhaust-steam should be utilized for heating up the feed, the milk of lime, &c.

The *milk of lime* is made in the two iron cylinders I and K, each about 6 feet high and 7 or 8 feet wide, which can be conveniently placed beneath the mud-settlers. I serves for slaking the lime and preparing the milk, K for storing the latter and also for the lime-pump L; it is sunk in the ground, so that the whole contents of I may run into L. Figures 119 and 120 show this arrangement on a large scale. A donkey-engine *a*, bolted to I, drives the agitators of both cylinders. In I there is a cage *b*, formed of perforated metal plates, for receiving the lime; it occupies a segment of an annular space in the upper third of I, one third or half round its circumference; the upper cross arm of the agitator is accordingly shortened. The cock *c* runs the milk of lime from I through the finely perforated zinc plate in the sieve *d*, and from this into K.

Fig. 119.

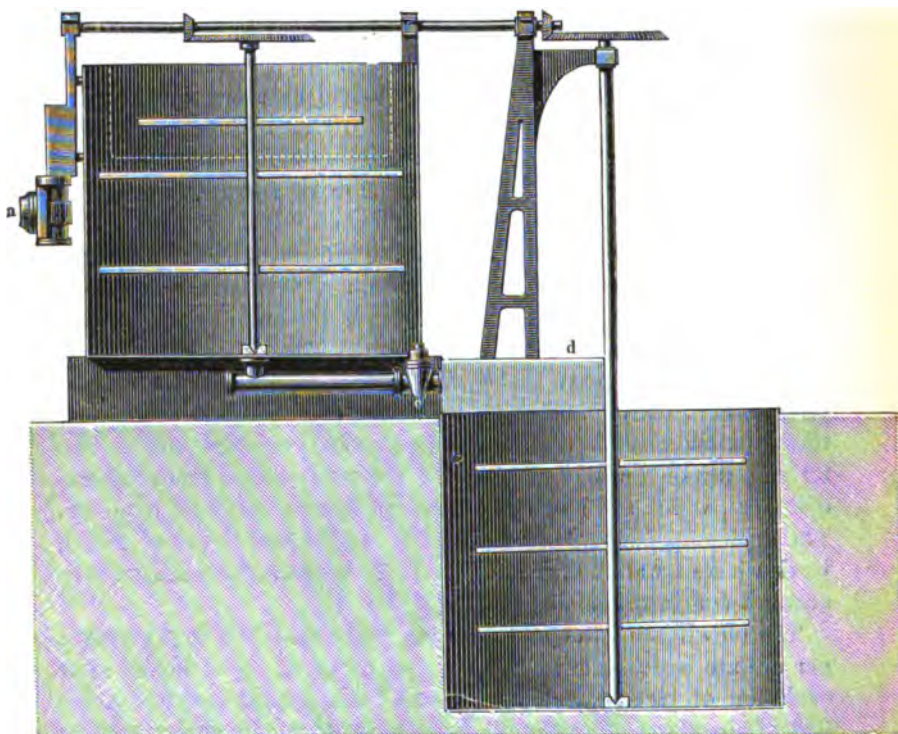
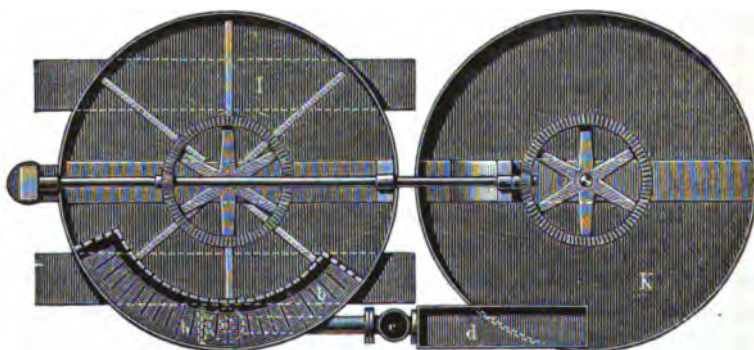


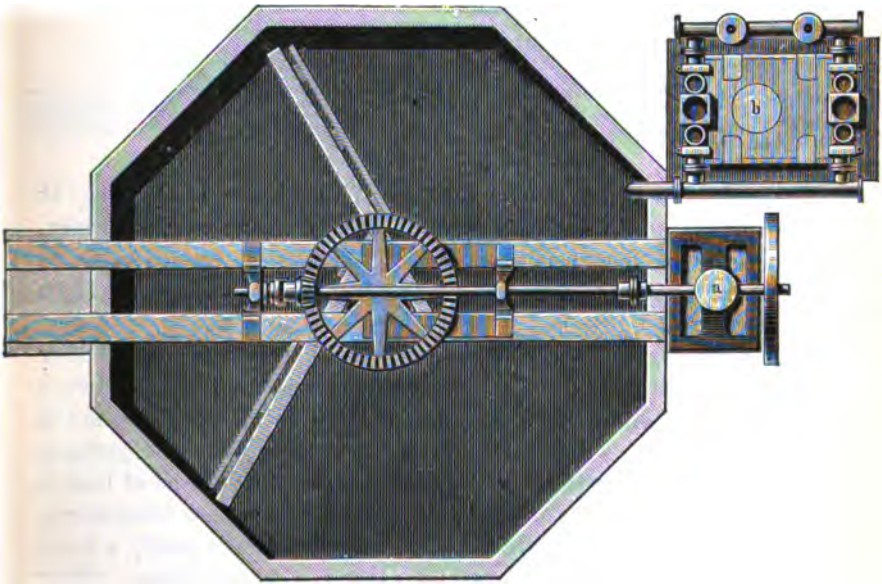
Fig. 120.





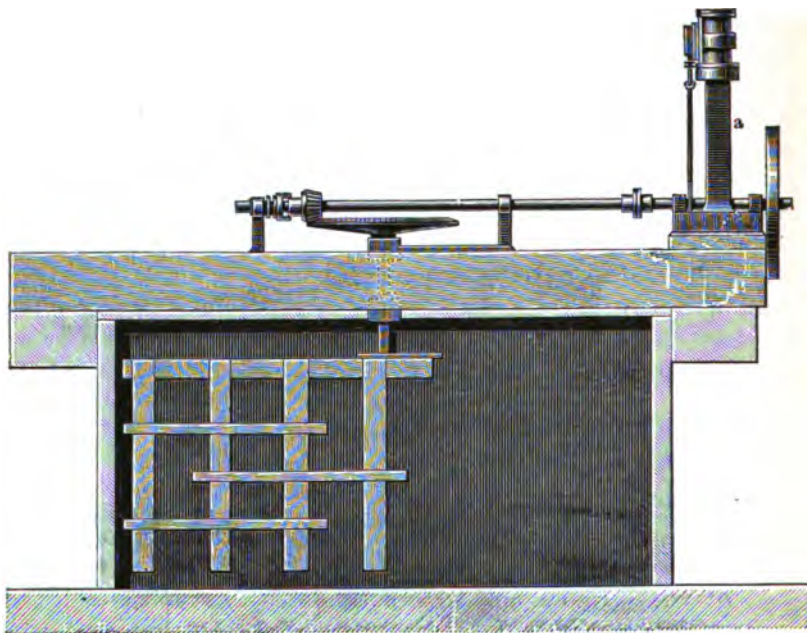
The *neutralizing-well* F (in figs. 116 and 117) is always sunk in the ground, and surrounded by a clay puddle in order to prevent the running-out of liquor as much as possible. It is either made of large stone slabs, in an octagonal shape, or of fire-bricks or hewn freestone, in a circular form. Of course the stone must be acid-proof and set in tar-pitch and sand in the most careful manner. At least once a week the well must be left filled for a night and exactly gauged, to control its being tight. A leak once formed, even if discovered, is very difficult to stop effectually. The well is covered with strong tarred planks, in which a large man-hole, a stoneware pipe for carrying the gas into the nearest chimney-flue, and a central aperture for the agitator are made. The latter is either suspended as in figs. 121 and 122 (where *a* is the

Fig. 121.



steam-engine for driving the agitator, *b* the pumping-engine for the manganese liquor), the agitator itself being made of wood and fastened in an iron upper part, or it is made more substantially with an iron shaft rotating in a footstep, as in fig. 117. The

Fig. 122.



latter does not easily give out, in spite of the mud lying at the bottom, and is not so frequently out of repair as the former. There are in large works several of these wells; but one suffices for the apparatus here represented, 5 feet 6 inches deep and 13 to 15 feet wide.

The *chlorine-stills* employed in the Weldon process widely differ in shape from those used in the ordinary process. They are always composed of stone flags, and are much larger, especially much higher, than the stills for manganese ore; they have no grating. The shape usual at small works (turning out 7 or 8 tons of bleach daily) is shown in figs. 123 and 124. Fig. 123 is a view from above, with a portion of the cover taken away; fig. 124 is partly a front and partly a sectional elevation. Upon a bottom-stone, about 8 feet 6 inches square and 10 to 12 inches thick, the four sides are erected in two tiers, one above the other. Fig. 125 shows the way in which the corners are joined together. Of course there is always a channel provided for the tar and china-clay cement ("black stuff"). The four sides are tied together by strong cast-



Fig. 123.

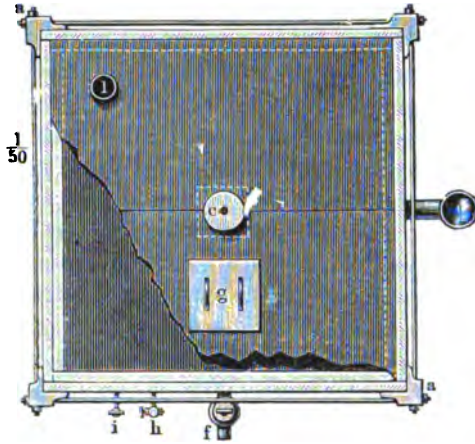
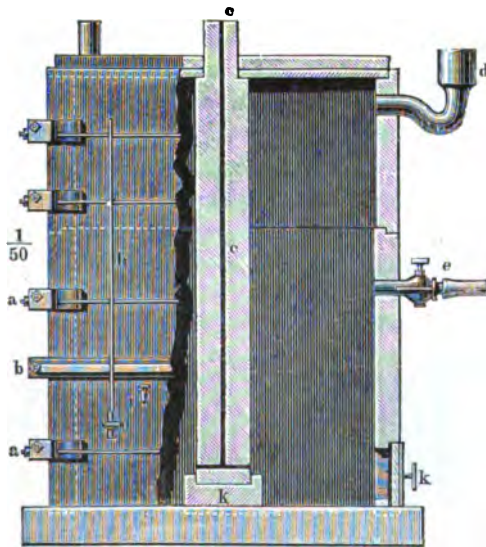


Fig. 124.



iron corner-brackets with screw-bolts passing through them, shown at *a a*; there are at least two sets of these for each tier. All iron work is thickly coated with coal-tar pitch; the corner-brackets do not touch the stone directly, but a piece of sheet lead is put in between; the screw-bolts are surrounded with india-rubber or

earthenware pipes at any place where they might be damaged by drops of acid. As the stills are exposed to pretty strong shaking during the steaming, and the joints may thus be loosened or even the stones be cracked, it is very useful to strengthen the lower tier in the way represented by bracing it with strong railway-plates pressing against the stones, a piece of sheet lead lying between; in the corners they are bent round in the way seen in fig. 125, and brought together by strong bolts. The steam-pipe *c* is made from a 16-inch-square stone column by drilling into it a central  $1\frac{1}{2}$ -inch hole, and close to the bottom three or four cross holes. At the bottom it rests in a stone socket *k*; at the top it is joined to a lead steam-pipe, continued into an iron one, the cock of which should be protected in the way described on p. 296. Instead of a stone column, at some works strong earthenware pipes of about 6 inches diameter and  $1\frac{1}{2}$  inch bore are employed; but these must be made in two pieces, as such long pipes (13 feet) cannot be made in one; and the joint is very difficult to keep tight. On the top the square steam-column is dressed in a circular shape, affording a support for the two halves of the top cover, which also rest in recesses of the side stones. The manganese mud is run in by a 6-inch-wide lead or stoneware funnel with swan-neck pipe, above which is arranged the sluice-valve of one of the branches of the mud-pipe from the mud-settlers. Several other hydraulic lutes are employed for the same purpose, often fixed on the cover itself as that shown in fig. 126. *e* (fig. 124) is the 3-inch stoneware

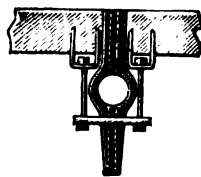
Fig. 125.



Fig. 126.



Fig. 127.



cock for feeding with acid; this may also be placed higher up, but not lower than one third of the height of the still from the bottom. This cock is kept tight against the stone by a contrivance shown on an enlarged scale in fig. 127. The cock should not be cemented

into the acid-pipes outside, but connected with them by an india-rubber pipe, as otherwise the shaking of the still easily loosens the joints of the pipes. A similar cock is fixed close above the bottom for discharging the manganese liquor at the end of the operation, unless it is preferred to employ a stoneware pipe continued into a 4-inch india-rubber pipe squeezed together by an iron clamp. Some manufacturers prefer this latter arrangement on account of the liability of earthenware cocks to break; but neither do the india-rubber pipes last long, and their renewal costs much more than that of the earthenware cocks. *g* is the lid of a man-hole for occasionally entering the still; another man-hole is made close above the bottom, and is closed by a wooden lid covered with a sheet of india-rubber, pressed against a recess of the stone by a screw-bolt arrangement. Neither man-hole need be opened frequently, as the still but rarely requires cleaning. There is also a stoneware pipe with outlet-cock for putting-in the glass liquor-gauge pipe *h* (which is kept tight in it by a bit of indiarubber tubing), also a small testing-cock, *i*, and a gas-pipe, *l*, on the top. That the stills should be erected on a most substantial foundation, hardly requires mentioning.

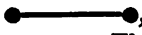
For large works the square shape of still is not so well adapted as the octagonal; for it is important, in regard to simplifying and superintending the work, to employ only a few stills, and consequently make them of much larger dimensions than those here stated; and this cannot very well be done with square stills, as stones of sufficient size would not be easily procurable. Such an octagonal still is represented in figs. 128 and 129, on a scale of 1 to 50; but at some works they are made even much larger, up to 12 feet wide and high. Fig. 128 is a view from the top, with part of the cover removed; fig. 129 a sectional elevation, omitting the ironwork. The bottoms in this case cannot be made of a single stone; they must be composed of two or four stones, bound together by corner-brackets and bolts, *a a*. The octagonal sides, also in two tiers, are joined at the corners by india-rubber cord, lying in shallow grooves of the adjoining faces (comp. the description, Vol. II. p. 334). Or else india-rubber bands with raised edges, like , are employed, and corresponding grooves made in the stones. The stones are bound together by the brackets *b b* and screw-bolts; sometimes by strong cable-chains, drawn up tight by coupling-screws. These do not press immediately upon the side-

Fig. 128.

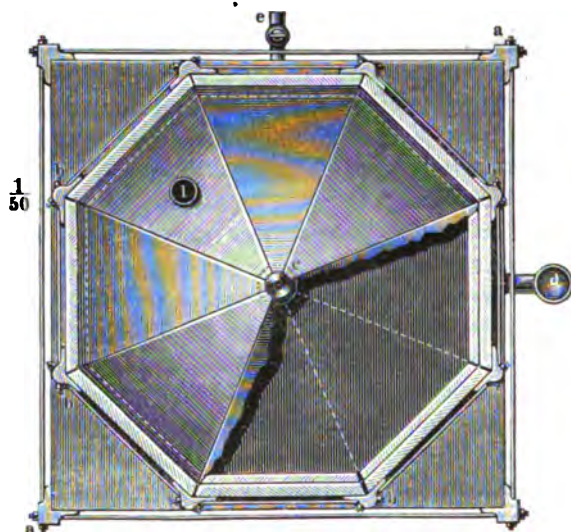
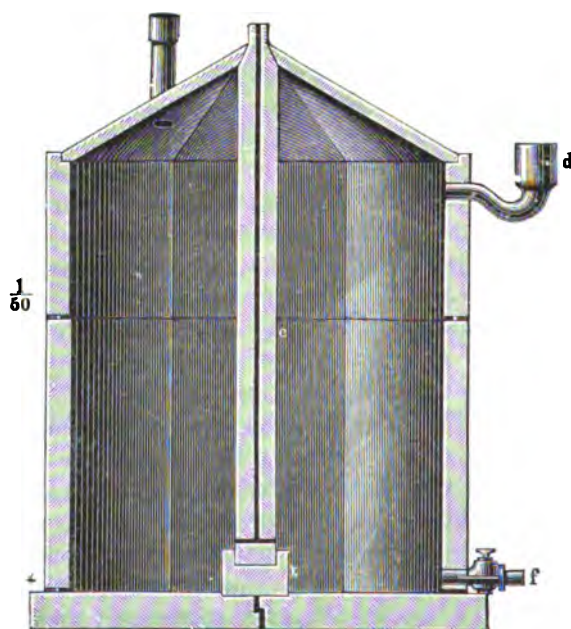


Fig. 129.



stones, but on strong wooden posts, of which two are provided for each of the eight sides, and from which the chains are at the same time suspended on pegs; perfect tension is secured by means of wedges. The top-cover is usually made dome-shaped; eight triangular stones rest with their bases in recesses of the side-stones; and their apices lean against the head of the stone steam-column *c*, shaped to suit this. The other parts represented here, and noted by the same letters as the similar parts of the square stills, require no explanation.

Fig. 130.



Fig. 130 shows a large hexagonal chlorine-still in a perspective view, which especially illustrates the iron bracings.

In the first edition of this work, vol. iii. pp. 212 & 213, the details of a contract for erecting a Weldon plant are given. As

these date from 1873, they must now be considered antiquated; and we shall only remark that this estimate, referring to a production of 6 or 7 tons bleaching-powder, came to a sum-total of £2877 4s. 7d. (inclusive of steam-boiler and shed for the same), but at the present day the plant could be erected much more cheaply.

We shall begin the description of the *work carried on in Weldon's chlorine-process* at the point where the acid still-liquor runs into the neutralizing-well, because in every case the process is commenced with such still-liquor, obtained from manganese ore in the ordinary way. The liquor must be first *neutralized* by adding calcium carbonate till all free acid has been saturated, and all iron precipitated as hydroxide. For this purpose ground chalk, limestone, lime riddings, &c. are employed; the more finely ground they are, the less excess of them is necessary, and the more quickly the work goes on. Since the mud left here is not merely worthless, but causes the principal loss of manganese by mechanical absorption, the smallest possible excess is desirable. Some factories employ milk of chalk made in a mortar-mill, by which the neutralization is accomplished at once and without any excess to speak of.

In the neutralizing, together with much carbonic acid, the free chlorine, never absent in still-liquors, is given off: hence the well must be kept covered and connected with the chimney by a stone-ware pipe. Too quick an addition of lime causes the liquor to froth over. The agitator must be constantly going round, and must be strongly built, as it suffers considerably. The process is finished when a sample of the liquor, poured on ground chalk, causes no effervescence.

For neutralizing still-liquor from native manganese ore very much limestone is required, up to four times the weight of the peroxide formed. This is avoided if the liquors from the native-manganese-stills are first run through the Weldon mud-stills, in which case their free HCl is usefully employed. With liquor from recovered peroxide 10 to 30 parts of ground chalk or limestone are required for 100 parts  $MnO_2$ , according to the degree of division.

The neutralized manganese liquor, along with the mud, is pumped up to the liquor-settlers H H (figs. 115 to 117). It is most important that it should become perfectly clear by subsidence; any mud remaining in suspension not merely contaminates the recovered peroxide by calcium sulphate (from the sulphuric acid contained in

the hydrochloric acid), calcium carbonate, ferric oxide, &c., but also very frequently causes the contents of the oxidizer to froth over during the blowing. With muddy liquors low-strength manganese mud with a high "base" is always obtained.

The settling mostly takes but a few hours; the clear liquor is then run, by carefully lowering the inner swivel-pipe, into one of the oxidizers, where it is just required. The mud can be left in the settlers H H till it has accumulated too much—which of course will happen much sooner or later according to circumstances, often after only two or three batches. It is then run off by opening the plugs *ll*, first to some vessel (not shown in the drawing) where it is left to subside again in order to draw off the clear manganese liquor as closely as possible; then it is often washed—but not too much, in order to avoid diluting the manganese liquor. The best effect is produced by filter-presses, which make any dilution unnecessary. On the more or less careful way of treating this waste mud the loss of manganese in the whole recovery-process chiefly depends.

Black (comp. p. 315) gives the following analysis of waste mud; but the large quantity of calcium carbonate in excess there shown would certainly have been avoided by better grinding and more careful employment of the chalk:—

	From native manganese.	From recovered peroxide.
CaSO <sub>4</sub> .....	0·68	0·46
CaCO <sub>3</sub> .....	35·64	55·15
MgCO <sub>3</sub> .....	0·29	0·75
CaCl <sub>2</sub> .....	6·06	5·71
MnCl <sub>2</sub> .....	2·41	1·38
Fe <sub>2</sub> O <sub>3</sub> .....	1·83	1·86
Al <sub>2</sub> O <sub>3</sub> .....	1·57	0·57
SiO <sub>2</sub> .....	1·17	2·10
H <sub>2</sub> O &c.....	50·35	32·02
	<hr/> 100·00	<hr/> 100·00

No MnO<sub>2</sub> is mentioned here, but this is really never absent in this waste mud. In 1890 the average at a well-conducted factory was 2·5 per cent. MnO<sub>2</sub>, 3·0 per cent. MnCl<sub>2</sub>, and 80 per cent. water.

The clear liquor standing over the mud averages 3.7 lb. per cubic foot, or 60 grams per litre, expressed in terms of  $\text{MnO}_2$ .

By a patent taken in 1877 (No. 638) I proposed a certain use for this waste mud—applied by me at least four years previously. It contains much ferric oxide and often even manganese peroxide, and is consequently eminently adapted for disinfecting the drainage from old tank-heaps. The way in which it can be employed for this purpose has been indicated in Vol. II. p. 854.

In many cases this mud contains a large proportion of *calcium sulphate*, nearly all owing to the sulphuric acid present in the hydrochloric acid employed in the chlorine manufacture, especially in the “roaster-acid” (Vol. II. p. 415). This sensibly increases the bulk of the mud, and thereby the mechanical loss of manganese. This is not the case with “pan-acid” (the mud analyzed by Black was of this kind), nor even with roaster-acid, if treated according to Weldon and Strype’s patent (No. 222, 1881; comp. Vol. II. p. 416) with calcium chloride (of which enormous quantities go to waste in the Weldon process), so as to precipitate the sulphuric acid in the shape of sulphate of lime. This requires about 20 vols. per cent. of the chloride-of-calcium liquor. The  $\text{CaSO}_4$  is separated by a filter, consisting of a bed of pebbles covered with sand, and is to be employed after washing as “pearl-hardening” (Vol. II. p. 721); but it is probably mostly thrown away. This process is especially useful in cases where the still-liquor has been neutralized, not with calcium carbonate, but with manganese mud (comp. below).

Wigg (No. 1220, 1882) patented the very old process of purifying the hydrochloric acid by barium chloride. The barium sulphate is to be fused with calcium chloride, and the barium chloride formed is to be quickly separated from the calcium sulphate by lixiviating at  $35^\circ \text{C}$ .

Weldon had proposed very early (pat. No. 732, 1869) to abandon the neutralization of still-liquor by calcium carbonate and replace it by treating it with *recovered manganese* (“Weldon mud,” comp. below) until neutralized. In this case the acid present in the still-liquor first saturates the “base” and leaves a purer  $\text{MnO}_2$  behind, which is suspended in the  $\text{MnCl}_2$  liquor and separated from it by settling. This saves the cost of limestone-dust and all the loss caused by “waste mud” (pp. 338 & 365). But this cannot be done except in the case of hydrochloric acid free from sulphuric



acid; for otherwise too much  $\text{CaSO}_4$  is mixed with the  $\text{MnO}_2$ . Hence the proposal, first to remove as much sulphuric acid as possible by  $\text{CaCl}_2$ , before employing the hydrochloric acid in the chlorine-stills, and then to neutralize the still-liquor with Weldon mud. But since the  $\text{CaCl}_2$  does not remove all the sulphuric acid from the hydrochloric acid, it is necessary from time to time to neutralize a batch of still-liquor by calcium carbonate, which causes all the accumulated sulphuric acid to be precipitated as  $\text{CaSO}_4$ . According to Weldon's statement it was found that, at a factory where the above process of purifying the hydrochloric acid was in operation, only one batch in forty needed to be neutralized with  $\text{CaCO}_3$  instead of with Weldon mud. But elsewhere less favourable experiences have been made. At all events that process requires the use of two neutralizing wells; nor does it remove the never absent quantities of iron, alumina, and silica, which must be got rid of in some way. Hence it did not meet with any extensive application for a long time.

Weldon's proposal of 1869 was repeated by G. E. Davis in 1883 (*Journ. Soc. Chem. Ind.* 1883, p. 155). By a special pamphlet, published in the same year, Weldon not merely claimed his priority, but strongly objected to most of Davis's calculations, and opposed the notion that the advantages of that process were as considerable as represented. He also declared Davis's proposal, to remove most of the calcium sulphate in the shape of crystals by cooling the still-liquor before neutralization, to be entirely impracticable.

That process, abandoned by Weldon himself, seems to have been laid aside for a long time. But in 1891 it was again revived, and in 1892 it seems to have become quite general in England, as shown by the Alkali Inspectors' Reports, xxviii. p. 44, and xxix. p. 66. It has thus become possible to make a ton of 35 per cent. bleach with considerably less than 45 cwt. of salt, to save the limestone-dust, and to avoid all nuisance by gases from the neutralizing-well.

*Precipitation of Manganese Protoxide from the Neutralized Liquor.*—The chloride-of-manganese liquor must now be treated with *lime*. For this very pure lime (free from magnesia especially) is required, which should be burnt down to a maximum of 2 per cent. of carbonic acid, but should not be overheated so as not to be

slaked easily and completely. The drawbacks connected with incomplete burning are self-evident; those of partially burning "dead" are, that the milk of lime, even after straining through fine wire gauze &c., contains many minute grains of unslaked and consequently chemically inactive lime, which cannot assist the operation in the oxidizers, but remains behind as injurious "base," causing a waste of hydrochloric acid. The proper state of the milk of lime is soon known from its uniform appearance and the absence of gritty particles in it. The damage done by magnesia, according to Weldon, is very great. Whilst most of the lime during the operation is converted into calcium chloride and its solution is afterwards mostly removed by decantation, the whole of the magnesia remains in the manganese mud as part of that portion of the "base" which is not combined with  $\text{MnO}_2$ . Having been converted in the stills into  $\text{MgCl}_2$ , it goes back to the oxidizer in that state. So long as any  $\text{MnCl}_2$  remains undecomposed, the  $\text{MgCl}_2$  remains undecomposed also; but the first effect of the excess of lime is to reconvert the  $\text{MgCl}_2$  into  $\text{MgO}$ , the quantity of which present is now increased by that arriving fresh with the lime. The magnesia thus constantly accumulates, causing the mud to become continually more and more basic, and thereby increasing the consumption both of acid and of lime, per unit of chlorine obtained, with every repetition of the operation. This evil may be, to some extent, avoided by using more than the normal quantity of final liquor, since, with time, after the  $\text{MnCl}_2$  of the final liquor has reacted on half the lime (see below) in the  $\text{CaOMnO}_2$ , it will react on any  $\text{MgO}$  present before reacting on  $\text{CaO}(\text{MnO}_2)_2$ , converting the  $\text{MgO}$  into  $\text{MgCl}_2$ , some of which will then be removed with the  $\text{CaCl}_2$ . This remedy, however, can at best be only partial, since merely a portion of the  $\text{CaCl}_2$  present with the mud, and therefore of any  $\text{MgCl}_2$  mixed with it, is decanted each time; and it is, moreover, very expensive, owing to the reaction of  $\text{MnCl}_2$  on  $\text{MgO}$  requiring too much time. It involves the risk, too, of impatient workmen running the batches off before the excess of  $\text{MnCl}_2$  has completely reacted, thereby occasioning excessive loss of manganese.

It is thus evident that those descriptions of lime which burn badly and contain over 1 per cent. magnesia or other impurities are not fit for the Weldon process. The lime intended for this purpose is not slaked in the ordinary way to a dry powder; it has been found

that much better and more active milk of lime is produced by introducing the quicklime directly into hot water. This is done in a cylindrical vessel with agitator (comp. figs. 119 and 120, p. 330); a strainer, formed of perforated metal plates, is fixed in the upper part of the vessel, into which the quicklime is put, and which retains stones and any other coarse impurities, while the circulating water washes out the finer particles. Before running into the storage-vessel, the milk of lime passes another strainer of finely perforated sheet zinc or wire gauze; in larger works this strainer is an inclined rotating cylinder, at the lower end of which the gritty particles are discharged, while the milk runs through the fine holes in the sides of the cylinder. The strained milk of lime ought to be as strong as possible, containing from 20 to 22½ lb. CaO per cubic foot.

Johnson and Hutchinson (Engl. pat. 8623, 1885) promote the formation of milk of lime and its separation from the impurities accumulating on the strainer by means of a jet of compressed air.

The following table shows the contents of lime in the milk according to specific gravities; it is valid for any lime of ordinary purity, at a temperature of 15°:—

Degrees Twaddell.	Grms. CaO per litre.	Lb. CaO per cubic foot.	Degrees Twaddell.	Grms. CaO per litre.	Lb. CaO per cubic foot.
2	11.7	0.7	28	177	11.1
4	24.4	1.5	30	190	11.9
6	37.1	2.3	32	203	12.7
8	49.8	3.1	34	216	13.5
10	62.5	3.9	36	229	14.3
12	75.2	4.7	38	242	15.1
14	87.9	5.5	40	255	15.9
16	100	6.3	42	268	16.7
18	113	7.1	44	281	17.6
20	126	7.9	46	294	18.4
22	138	8.7	48	307	19.2
24	152	9.5	50	321	20.0
26	164	10.3			

In testing the following precautions must be observed:—The milk of lime is placed in a somewhat wide cylinder, the hydrometer is gently inserted, and the cylinder is slowly turned round on the table, so as to undergo a slight shaking. The hydrometer then slowly sinks down, and the reading is taken when it stops. If

simply inserted into thick cream of lime, it stops at any point. In the case of thin milk, on the other hand, the reading must be taken quickly, before the lime settles down.

Supposing there is a stock of well-settled manganese liquor and properly made milk of lime on hand, one of the oxidizers is half-filled with manganese liquor, of which a large quantity must be in reserve in one of the settlers H H. Under normal circumstances the manganese liquor would be strong enough to correspond to about  $3\frac{1}{2}$  lb.  $MnO_2$  per cubic foot. It is heated by blowing in steam to  $55^\circ C.$ , and milk of lime run in while the blast commences to work slowly. The milk of lime is contained in a gauged tank; and its initial level is exactly noted. When the point has been approached at which all manganese has been precipitated, constant testings are made; and the supply of lime is stopped as soon as that point has been reached. The testing is done by taking small samples of liquor (well mixed by the blast) from the small cock in the oxidizer in or near the testing-cabin (p. 327), filtering them, and trying the filtrate for alkaline reaction by red litmus-paper. This indicates very accurately any excess of lime, which is much more soluble in a solution of  $CaCl_2$  than in pure water, at least at a temperature of  $50^\circ$  or  $60^\circ C.$  The filtrate is also tested with strong bleach-liquor, by which no brown colour (from  $MnO_2$ ) must be produced. In many factories the milk of lime is pumped directly from the vessel K (fig. 120), which is provided with a liquor-gauge, into the oxidizer. In this case the pumping must cease directly the point of neutrality has been reached: the level of the milk of lime in K is read off, and the third or fourth, &c., still needed (see below) is pumped in. It is much safer and more convenient to pump the milk of lime at once into the tank M, fixed above the oxidizers, or at least at the height of the settlers H H; from this the milk of lime, by means of a valve accessible from below, is run slowly or quickly, as it may be required, into the oxidizer, and that by the man in the testing-cabin, who is thus independent of the man at the pump. In any case the number of measures of milk of lime used is read off, and a quarter or a third of the quantity used is run in in excess. Evidently any error exceeding the point of precipitation in the first addition must cause three or four times as much error in the second addition. Some works only add one fifth. This depends on the nature of the lime, the strength of the liquors, and other circumstances not quite explained; but under

like conditions the same excess is always required, as is proved by the quantity of "final liquor" used at a later stage. When working with liquors from native manganese, *i. e.* starting the process from the first, the second addition of lime should not be made all at once, but in several portions at intervals of a quarter of an hour, lest a "stiff batch" be produced.

*Blowing.*—As soon as the second addition of lime has been made, *i. e.* as quickly as possible after precipitating the manganese as  $\text{MnO}$ , the blast is put on with full strength and kept at this; otherwise a "stiff batch" would be produced, as inversely a "red batch" is formed when the blast is put on fully before the lime has been put on. We shall discuss these phenomena later on. At this stage the contents of the oxidizer consist of a mixture of hydrated manganese protoxide and free calcium hydrate, the former suspended, and the latter partly suspended and partly dissolved, in solution of calcium chloride. The chief reason why an excess of lime is added is the fact, discovered by Weldon, that when manganese hydroxide is treated by atmospheric air in presence of a soluble base, very much more of it is converted into  $\text{MnO}_2$ , and that in very much less time, than when manganese hydroxide alone is so treated. At the temperature actually employed in the Weldon oxidizer, in the absence of any base other than itself, only one third of the  $\text{Mn(OH)}_2$  would become peroxidized, the product being red oxide, or  $\text{Mn}_2\text{O}_3$ ; if the operation were performed at the temperature of the atmosphere, and the treatment with air continued sufficiently long, one half of the  $\text{Mn(OH)}_2$  would become converted into  $\text{MnO}_2$ , but not more than half, however long the treatment with air might be continued. The product of the treatment of  $\text{Mn(OH)}_2$  alone by air in the wet way is thus always a "manganite of manganese"—either  $\text{Mn}_2\text{O}_3$ , consisting of one of  $\text{MnO}$ , combined with two of  $\text{MnO}$ , or  $\text{Mn}_2\text{O}_3$ , consisting of one of  $\text{MnO}$ , combined with one of  $\text{MnO}$ , according to the temperature at which the operation is performed. The fact that the whole of the  $\text{Mn(OH)}_2$  can be converted into  $\text{MnO}_2$ , if a full equivalent of lime be present, Weldon explains as being due to  $\text{CaO}$  replacing, and so permitting to become peroxidized, the  $\text{MnO}$  which would otherwise become locked up in combination with  $\text{MnO}_2$ .

The principal advantage of this displacement of  $\text{MnO}$  by  $\text{CaO}$  consists in the fact, already referred to, that to obtain a given

quantity of  $\text{MnO}_2$  in the state of calcium manganites requires less than a tenth of the time, and consequently less than a tenth of the coal, and less than a tenth of the apparatus, which would be required to obtain the same quantity of  $\text{MnO}_2$  as  $\text{Mn}_2\text{O}_3$ . While  $\text{MnO}_2$ , recovered from still-liquors in the state of calcium manganites, is very much less costly than native manganese ore,  $\text{MnO}_2$ , similarly recovered as  $\text{Mn}_2\text{O}_3$  would thus be very much more costly than native manganese. But this substitution of  $\text{CaO}$  for  $\text{MnO}$  has a further advantage. While the richest product which can be obtained by treating  $\text{Mn}(\text{OH})_2$  alone by air in the wet way is  $\text{Mn}_2\text{O}_3$ , containing a full equivalent of combined "base," and so consuming  $6\text{HCl}$  per  $2\text{Cl}$  liberated by it



a portion at any rate of the Weldon product consists of an "acid manganite,"  $\text{CaO}(\text{MnO}_2)_2$ , or  $\text{CaMn}_2\text{O}_6$ , which consumes one-sixth less acid than  $\text{Mn}_2\text{O}_3$  consumes, giving  $4\text{Cl}$  for  $10\text{HCl}$ :



The proportion of this acid manganite is sometimes sufficient to reduce the "base" in the Weldon product to 0.6 of an equivalent per 1.0 equivalent of  $\text{MnO}_2$ , but the combined base together with the basic bodies not combined with  $\text{MnO}_2$ , but present as accidental impurities, more usually amounts to 0.7. With 0.7 of base, however, the Weldon product consumes only 5.4  $\text{HCl}$  for each  $6\text{HCl}$  which would be required by  $\text{Mn}_2\text{O}_3$ ; while its regeneration moreover requires only 1.7  $\text{CaO}$  per 1.0 of  $\text{MnO}_2$  in it, instead of the 2.0  $\text{CaO}$  which would be required for the production from  $2\text{MnCl}_2$  of 1.0 of  $\text{MnO}_2$  as  $\text{Mn}_2\text{O}_3$ .

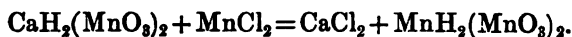
A consumption of 5.4  $\text{HCl}$  per 2  $\text{Cl}$  is much greater than that calculated for pure  $\text{MnO}_2$ . But manganese peroxide very rarely occurs in nature free from lower manganese oxides and other matters absorbing acid, especially ferric oxide; and such pure ore is not at all accessible to the bleaching-powder-maker, owing to its high price. Actually, in the *best* case as much acid is required with native manganese as with the regenerated peroxide, and nearly always much more with the former, because incomparably more free acid must be left in the still-liquors than when the thin mud of recovered peroxides is made use of.

The "manganites" always cited in the Weldon process have

certainly never been examined in a pure and absolute state ; they are in any case amorphous compounds, always mixed with impurities. But there are some good reasons for assuming that such compounds do exist ; for it has been noticed that, in the action of  $\text{MnCl}_2$  in excess upon the compound  $\text{CaO}, \text{MnO}_2$  (or a mixture equivalent to this in composition, one of which must be formed in the Weldon process), one half of the  $\text{CaO}$  acts differently from the other half. Two reactions in fact take place, one instantaneously, the other requiring much time. The first furnishes acid calcium manganite and free  $\text{Mn}(\text{OH})_2$  :



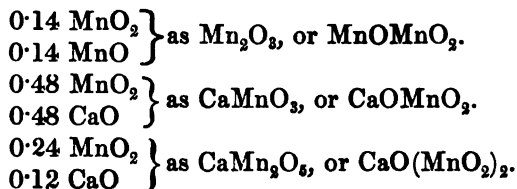
The other produces no free  $\text{Mn}(\text{OH})_2$ , but simply converts  $\text{CaH}_2(\text{MnO}_3)_2$  into the corresponding manganite of manganese :



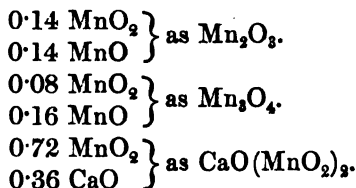
The acid properties have been denied by Post (Ber. d. deutsch. chem. Ges. 1879, pp. 1454, 1539 ; Verh. Ver. Gewerbeff. 1879, p. 464 ; Dingl. Journ. ccxxxvi. p. 225, ccxxxix. p. 74). His papers have been completely refuted by Weldon (Chem. News, xli. pp. 129, 179, 181 ; xlii. pp. 10, 19) and myself (Dingl. Journ. ccxxxv. p. 300 ; ccxxxvi. pp. 231, 236 ; ccxlii. p. 371) ; also indirectly by the numerous papers of other chemists, Rammelsberg, Stingl and Morawsky, Wright and Mencken, van Bemmelen, and especially Gorgeu, all of whom have proved the acid nature of  $\text{MnO}_2$  beyond contradiction.

While, by using a full equivalent of excess of lime in the Weldon process, the whole of the  $\text{Mn}(\text{OH})_2$ , or the whole of it within 1 or 2 per cent., can be converted into  $\text{MnO}_2$ , a full equivalent of excess of lime is never now used in practice. The use of so large an excess would be too apt to give "stiff batches" (see below), and would have no corresponding advantage. It would yield a product consisting almost entirely of  $\text{CaOMnO}_2$ , and so containing a full equivalent of combined base ; and although this might be reduced to 0.7 by acting on one half of the lime in that compound by  $\text{MnCl}_2$ , and oxidizing the resulting free  $\text{Mn}(\text{OH})_2$ , the quantity of final  $\text{MnCl}_2$  required would be inconveniently large. It is found better to use only from 0.6 to 0.7 of excess of lime ; and in the best-managed works the proportion of excess used is never less than 0.6 or greater than 0.7, whether the nominal excess be one half, as in works where the lime is of such quality that the manganese

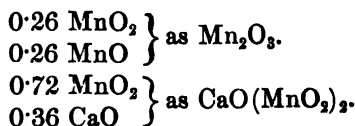
is all precipitated by about 1.1 eq. CaO, or whether it be only one fifth, as in works using a description of lime acting so much less readily that 1.3 to 1.4 eq. has to be added before the manganese is completely precipitated. With 0.6 eq. of excess of lime, the degree of oxidation obtained is usually about 86 per cent., the product, before the final liquor, consisting, in Weldon's view, of:—



Such a product contains  $0.14 + 0.48 + 0.12 = 0.74$  total protoxides per  $0.14 + 0.48 + 0.24 = 0.86 \text{ MnO}_2$ , or 0.86 eq. "base" per eq. of  $\text{MnO}_2$ . If  $\text{MnCl}_2$  be added to it until the filtrate from a sample gives a manganese reaction, it will decompose 0.24 eq.  $\text{MnCl}_2$ , being the quantity corresponding to one half the lime in its 0.48 of  $\text{CaOMnO}$ . If the treatment by air be then continued until absorption of oxygen ceases, the 0.24 of further  $\text{Mn(OH)}_2$  so obtained will become  $\text{Mn}_3\text{O}_4$ , or  $\text{Mn}_2\text{O}_3$ , according to temperature. If it becomes  $\text{Mn}_3\text{O}_4$ , the final product will consist of:—



If the  $\text{Mn(OH)}_2$  becomes  $\text{Mn}_2\text{O}_3$ , the final product will consist of:—



The base in the former case will be  $0.14 + 0.16 + 0.36 = 0.66$  per  $0.14 + 0.08 + 0.72 = 0.94 \text{ MnO}_2$ , or 0.7 eq. per eq.  $\text{MnO}_2$ , while the average degree of oxidation will have been reduced from 86 per



cent. before final liquor to 75·8 per cent. at the end of the operation. In the latter case, the final base will be  $0\cdot26 + 0\cdot36 = 0\cdot62$  per  $0\cdot26 + 0\cdot72 = 0\cdot98$   $\text{MnO}_2$ , or  $0\cdot632$  per eq.  $\text{MnO}_2$ , and the average degree of oxidation at the end will be 79 per cent.

The proportions of base here spoken of refer only to the *combined* base. There are always present, however, as impurities, basic bodies not combined with  $\text{MnO}_2$ , and especially small quantities of  $\text{MgO}$  and  $\text{CaCO}_3$ . The total "base," as shown by the ordinary methods of testing Weldon mud, includes these impurities. These impurities should never be present in sufficient quantity to raise the total base above 0·7.

The quantity of lime which must be run into the oxidizer, before a filtered sample ceases to give the manganese-reaction with bleaching-powder, differs according to circumstances, but always exceeds the exact equivalent of the manganese present. Freshly precipitated  $\text{Mn}(\text{OH})_2$  is soluble to a sensible extent in a neutral solution of calcium chloride, and is indicated by bleaching-powder and other reagents. Hence the reaction with bleach-liquor only ceases when a certain amount of lime over and above the equivalent has been added, and thus oxychloride has been formed. Moreover all the molecules of  $\text{CaO}$  in the milk of lime do not take part in the reaction upon manganous chloride: there are always coarser particles present, which, during the few minutes occupied by the precipitating process, have no time to act upon  $\text{MnCl}_2$ . But these coarser particles of lime are afterwards entirely dissolved in the hot solution of calcium chloride, and contribute to form the "base" of the manganese during the blowing. According to the quality of the lime, its degree of hydration and division, and the more or less careful straining, a different excess of it will be required before the manganese reaction ceases to be produced in a filtered sample. The minimum of lime required for this is 1·1, the maximum 1·45 equivalent. It is best, as has been said, not to employ less than 1·6 equivalent of lime; only then is a well-settling mud obtained, from which more calcium-chloride liquor can be drawn off than from a mud not settling so well. Thus a stronger mud (containing more  $\text{MnO}_2$  in a given bulk) is obtained for the chlorine-stills than by employing less lime. This is very important, even more so than a very low base, because it saves coals, acids, space, and labour, and less manganese is lost. Usually from 12 cwt. to 14 cwt. of lime per ton of bleaching-powder are required for the recovery

process (*i. e.* about as much as in the bleaching-powder boxes). These quantities include the portion which is sifted out in making the milk of lime, and which thus does not go into the oxidizer. According to the quality of the lime employed, more is sifted out in some works than in others.

The *calcium chloride* always present in Weldon liquors plays a most important part in the process, as Weldon himself pointed out at an early period. At well-managed factories they regularly test the liquors for  $\text{CaCl}_2$ , and in case of need add some of this salt. Where it is deficient, "stiff batches" are the consequence. At Aussig, *e. g.*, I found that the rule was to keep to  $2\frac{1}{2}$  mols.  $\text{CaCl}_2$  for each mol.  $\text{MnCl}_2$ .

The Salzbergwerk Neu-Stassfurt (Germ. pat. 53756) feeds the  $\text{HCl}$ -condensers, connected with the salt-cake furnaces, with a solution containing 15 per cent.  $\text{CaCl}_2$ , in order to introduce more of this salt than usual in the Weldon process.

The first accurate investigation on the part played by calcium chloride in the Weldon process was made by myself together with Zahorsky (Zsch. f. angew. Chem. 1892, p. 631). The first consideration is that a  $\text{CaCl}_2$  solution dissolves more lime than pure water, which must promote the oxidation. Since no exact observations on the solubility of  $\text{CaO}$  in  $\text{CaCl}_2$  solutions were available, this want was supplied by constructing the following table:—

*Solubility of Lime in solutions of Calcium Chloride at different Temperatures, in terms of grams  $\text{CaO}$  per 100 cub. cent. solution.*

Percentage of $\text{CaCl}_2$ in solution.	20°.	40°.	60°.	80°.	100°.
0 % $\text{CaCl}_2$ .....	0.1374	0.1162	0.1026	0.0845	0.0664
5 " .....	0.1370	0.1160	0.1020	0.0936	0.0906
10 " .....	0.1661	0.1419	0.1313	0.1328	0.1389
15 " .....	0.1993	0.1781	0.1706	0.1736	0.1842
20 " .....	0.1857*	0.2249	0.2204	0.2295	0.2325
25 " .....	0.1661*	0.3020*	0.2989	0.3261	0.3714
30 " .....	0.1630*	0.3684*	0.3664	0.4112	0.4922

(In the cases marked with an asterisk a precipitate of calcium oxychloride was formed, which removed some  $\text{CaCl}_2$  from the solution.)

The solubility of lime in solutions containing up to 10 per cent.  $\text{CaCl}_2$  at ordinary or slightly raised temperatures does not differ

much from that in pure water, no oxychloride being formed. At higher temperatures more  $\text{CaO}$  is dissolved, and this increases even more with the concentration of the  $\text{CaCl}_2$  solution, until the state of matters is modified by a precipitation of solid oxychloride.

The dissolving-power of  $\text{CaCl}_2$  solution for  $\text{MnO}$  and  $\text{MnO}_2$  will be mentioned later on.

Our experiments were made in the laboratory with the aid of a small blowing-engine, under conditions as nearly as possible equivalent to those of actual work; at all events they led to results capable of comparison. Owing to the lesser depth of layer, the oxidation took more time than on the large scale, viz. 10 hours, but the results were equal to the best obtainable in actual work. The experiments (which are described in detail *loc. cit.*) showed, to our surprise, that in the *first* stage of the process the oxidation, that is the formation of calcium manganite, took place all the more slowly the more  $\text{CaCl}_2$  was present, *e. g.* with 1 mol.  $\text{CaCl}_2$  six times as fast as with 6 mols. But this changes steadily as the blowing goes on; after six hours an equilibrium is reached, and up to 10 hours the *degree of oxidation regularly increases with the quantity of  $\text{CaCl}_2$  present*. With 1 mol.  $\text{CaCl}_2$  77.25 per cent. of the Mn was converted into  $\text{MnO}_2$ , with 3 mols.  $\text{CaCl}_2$  83.3 per cent., with 6 mols. 85.5 per cent., and on further two hours' blowing 89.13 per cent.

This leads to the conclusion (with all the reserve necessary in comparing our results with work on the large scale) that the best proportion is 3 mols.  $\text{CaCl}_2$  for 1 Mn. Below 3 mols. the oxidation is too slow; to add more is troublesome and increases but slightly the percentage of  $\text{MnCl}_2$ , unless the time of blowing is increased as well, which is not sufficiently profitable.

If this useful action of the  $\text{CaCl}_2$  were a consequence of its dissolving-power for  $\text{CaO}$ , other substances acting similarly on  $\text{CaO}$  ought to promote the oxidation in the same way. But experiments made in this direction with  $\text{KCl}$  and  $\text{NaCl}$  yielded *negative* results.

We must therefore take into consideration the solubility of manganese protoxide in  $\text{CaCl}_2$  liquors, which has been already observed by Weldon (*Chem. News*, 1869, xx. p. 109), and which we have confirmed with the addition that the solubility of  $\text{Mn(OH)}_2$  increases with the percentage of  $\text{CaCl}_2$ , colourless solutions being

formed. Weldon observed that the further oxidation of the *mechanically suspended* protoxide is retarded by the presence of dissolved  $\text{MnO}$  compounds; the contrary takes place if at the same time  $\text{CaO}$  is present. In this case "port-wine coloured" solutions are formed, which Weldon took to be solutions of calcium manganite in a solution of calcium oxychloride. We examined these liquids more closely, and we found that we have here not a simple solution, but probably a manganese dioxy-chloride,  $\text{Cl-Mn-O}_2\text{-Mn-Cl}$ , is formed. The opposite behaviour of solutions of  $\text{MnO}$  and  $\text{MnO}_2$  in  $\text{CaCl}_2$  during the oxidation of  $\text{MnO}$  by  $\text{O}$  led us to the following explanation of the action of  $\text{CaCl}_2$ , which at first retards, and afterwards hastens the process.

The  $\text{CaCl}_2$  dissolves part of the suspended  $\text{Mn(OH)}_2$ , and the latter then retards the oxidation of the undissolved  $\text{Mn(OH)}_2$ . The more  $\text{CaCl}_2$  is present the more  $\text{Mn(OH)}_2$  is dissolved and the more its retarding effect comes into play. But as the oxidation still proceeds, gradually the  $\text{MnO}_2$ , or rather the  $\text{CaMnO}_3$ , increases; it is partially dissolved, and yields the "port-wine solutions" in which the oxidation is *hastened*. Thus after a certain time the retarding action of the dissolved  $\text{MnO}$  is paralyzed by the quickening action of the dissolved  $\text{MnO}_2$ , and ultimately the latter prevails over the former. In that stage, as more  $\text{MnO}$  is dissolved the more  $\text{CaCl}_2$  is present, the rate of oxidation must increase with an increase in the quantity of  $\text{CaCl}_2$ .

A further step in the investigation of the part played by the  $\text{CaCl}_2$  has been made by J. Wiernik (Zsch. f. angew. Chem. 1894, p. 257), who based his conclusions on analyses of charges obtained on the large scale with liquors containing from 1.92 to 2.2 mols.  $\text{CaCl}_2$  to 1 mol.  $\text{MnCl}_2$ . He showed that the rate of oxidation is not influenced by the concentration of the manganese liquor, nor by the concentration or the rate of addition of the milk of lime. The percentage of  $\text{MnO}_2$  is not *directly* dependent on that of the  $\text{CaCl}_2$  in the liquors, but (apart from the intensity of the current of air) upon the quantity of the *lime*, and therefore *indirectly also upon that of calcium chloride*, as the quantity of lime cannot be increased by itself, on account of the danger of "stiff batches," unless at the same time that of  $\text{CaCl}_2$  is increased. *Practically*, therefore, an increase of  $\text{CaCl}_2$  is useful, as in this case more lime can be employed, much more  $\text{MnO}_2$  can be formed, and proper settling can be obtained without excessive blowing. Concerning

the manner in which the  $\text{CaCl}_2$  exerts its action, Wiernik agrees with the explanation given by myself and Zahorsky.

*Finishing the charge.*—We now revert to the commencement of the operation in the oxidizer. Supposing the proper amount of lime to have been added, the *blowing* is continued till the formation of  $\text{MnO}_2$  ceases. The colour of the thin mud, at first light yellow, changes into brown and finally into deep black. The oxidation goes on more or less quickly, according to the proportion borne by the volume of air blown in to that of the mass treated; but it is a general experience that the final result is much more favourable when a very strong current of air is applied,—and that a longer application of a less powerful current of air does not act so well, even if the total bulk of air forced through is the same. Hence much stronger blowing-engines are employed now than formerly (p. 329). Of course the efficiency of the blast increases with the depth of the mass to be treated, and with the quantity of  $\text{MnO}$  contained in a given bulk of the same. Under favourable circumstances an hour's work of 40 to 45 H.P. in the blowing-engine suffices for regenerating as much peroxide as will turn out one ton of 37-per-cent. bleach (comp. p. 329). For one ton of actual  $\text{MnO}_2$ , with very good work, 280,000 cubic feet of air are required, containing 58,800 cubic feet of oxygen. Weldon cites cases where to a ton of  $\text{MnO}_2$ , 270,000, 158,000, and 180,000 cubic feet of air are required, *i. e.* much less than just stated; but these figures refer to very deep oxidizers. On the other hand, frequently twice as much air is used, *viz.* 600,000 cubic feet.

When the process is first started, testings have to be performed every half-hour during the whole operation, in the manner to be described below, in order to observe whether the formation of  $\text{MnO}_2$  is still proceeding; this is not essential afterwards, as it is then known how long it is necessary to blow. In the apparatus formerly worked by myself the limit of this period was reached after three hours; but with other apparatus it may take two or five hours, according to circumstances; three to four hours is the average with smaller, two and a half hours with large blowing-engines. The alkaline reaction (which must always be sought for in the *filtrate* from a sample) should be quite perceptible for at least an hour after the commencement of blowing; afterwards it is weaker; and it should entirely cease towards the end of this first

period. If it ceases too soon, there has been too little excess of lime; if it does not cease at all, there has been too much. But the last-mentioned fault can be corrected in the now commencing final stage by an increased addition of "final liquor." We have seen above that there must be always a good stock of settled manganese liquor reserved at a sufficient height.

When the  $\text{MnO}_2$  in the mixture no longer increases, some more chloride-of-manganese liquor is run in, without stopping the blast; this is the "*final liquor*." Its object is to act upon half the lime existing as  $\text{CaMnO}_3$ , according to the equation



and thus to reduce the base, by obtaining, without using more lime, more protoxide of manganese, which is afterwards converted into a higher oxide. The final liquor is first added until the filtrate from a sample of the mixture gives the brown manganese reaction with bleach-liquor; this reaction ceases after a few minutes, all dissolved manganese having been precipitated. Then a little more final liquor is added, and the blowing continued till the filtrate from a further sample ceases to be coloured by bleach-liquor; and this is continued till it is seen, from the time which it takes to "blow out" the manganese, that the limit is reached. Now the blowing is continued a little longer, till the filtrate remains undoubtedly clear when bleach-liquor is added; and at last the whole contents of the oxidizer are discharged into one of the settlers. In my case this final period regularly lasted  $1\frac{1}{2}$  hour; so that the whole operation, from commencing the blowing proper to running off, took  $4\frac{1}{2}$  hours. If even the first final liquor cannot be easily "blown out," it is a sign of too little lime; if, on the other hand, very much final liquor is used, there has been too much lime; and these things have to be rectified in the next batch. The total amount of  $\text{MnO}_2$  per cubic foot is not always increased in the final stages; sometimes it is even lowered; but the base is always diminished.

The progress of the oxidation will be made clear by the following statements. Commencing with a manganese liquor containing  $\text{MnCl}_2$ , corresponding to 3.2 lb.  $\text{MnO}_2$  (=possible  $\text{MnO}_2$ ), this would be diluted about  $\frac{1}{4}$  by the steam and the milk of lime. After one hour's blowing, 1.02 lb.  $\text{MnO}_2$  per cubic foot is found; after  $1\frac{1}{2}$  hour,

1·6 lb.; after 2 hours, 1·85 to 2·05 lb.; after  $2\frac{1}{2}$  hours, 2·05 to 2·3 lb.; after 3 hours about the same quantity. The base is now about 0·8 or 0·9. Now the final liquor is added; and after  $4\frac{1}{2}$  hours there are 2·25 to 2·3 lb.  $\text{MnO}_2$  per cubic foot; the base is = 0·67. Below 0·6 base it is not easy to get; above 0·75 the work is decidedly bad. The above strength would correspond to about 80 per cent. of all the manganese being present as  $\text{MnO}_2$ , the remaining 20 per cent. as  $\text{MnO}$ . At a very well conducted English factory visited by me in 1890 the average percentage of  $\text{MnO}_2$  was  $2\frac{1}{2}$  lb. per cubic foot (60 grms. per litre), the base 0·7, and the degree of oxidation = 77 or 78 per cent.

All that now remains is the *concentration of the manganese mud*, which otherwise would become indefinitely diluted by the acid, the milk of lime, &c. The contents of the oxidizer are run past the valve *n*, through the main pipe *e e*, into one of the mud-settlers S S (figs. 115–117). Under normal conditions the thin mud separates after a few hours into a clear solution of calcium-chloride liquor and thicker mud; waiting for several days would not make much difference, and would require much more plant and ground. The clear liquor is drawn off by the pipe *i*, turning round a swivel inside the settlers and continued outside. When it is in its upright position, nothing runs out; and by gradually lowering it the clear  $\text{CaCl}_2$  liquor can be run off without disturbing the sediment. The  $\text{CaCl}_2$  liquor ought never to be run to waste straight from the settlers, but should always pass through a catch-well, say one or two large tubs, in which the movement of the liquor is very much retarded; at the bottom of these tubs gradually a good deal of peroxide mud accumulates. The thicker mud contains at least twice, and may even contain three times as much  $\text{MnO}_2$  as the thinner (up to 7 lb. per cubic foot); it is still liquid enough to be run for a hundred yards in 4-inch pipes, if this should be necessary from local circumstances.

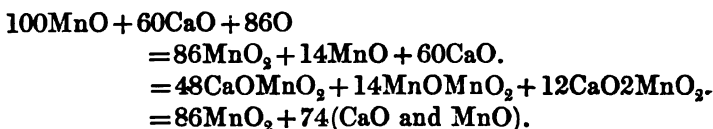
The *operations in the oxidizer* may be represented in the following way, neglecting the fact that from the commencement the liquor contains some calcium chloride. All numbers are to be understood as denoting equivalents, not simple weights.

1st operation: Charging the oxidizer and adding the lime.



2A 2

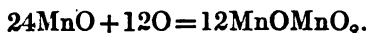
2nd operation : Blowing.



3rd operation : Adding the final liquor.



4th operation : Second blowing.



Apart from calcium chloride, there remain :—

from the 2nd operation,	14MnOMnO <sub>2</sub> + 12CaO <sub>2</sub> MnO <sub>2</sub> ;
"    3rd    "	24CaO <sub>2</sub> MnO <sub>2</sub> ;
"    4th    "	12MnOMnO <sub>2</sub> ;
altogether	26MnOMnO <sub>2</sub> + 36CaO <sub>2</sub> MnO <sub>2</sub> ,
or	98MnO <sub>2</sub> + 36CaO + 26MnO.

Hence upon 100 equivalents of manganous oxide originally employed, and 24 added later on, there are obtained :—

1st, 98 equiv. MnO<sub>2</sub>, instead of 124 possible, *i. e.* about 79 per cent.

2nd, 62 equiv. bases, viz. 36CaO and 26MnO.

By adding the final liquor, the proportion of MnO<sub>2</sub> to MnO has been lowered from 86 to 79 per cent.; but the bases have been diminished even more, viz. from 74 to 62.

Now and then in oxidizing two *faulty kinds of operations* occur, which are very awkward and spoil the batch. Batches thus affected are known as "red" or "foxy," and "thick" or "stiff." A *red batch* happens when the mixture turns brown-red instead of black. In this case nearly all the manganese is present as Mn<sub>3</sub>O<sub>4</sub>, or only 25 per cent. of all possible MnO<sub>2</sub> is present as such, 75 per cent. as MnO. This kind of thing occurs when the blast is working at full strength before any excess of lime has been added to the liquor. When once a charge has turned red, there are no means known of putting it right: no amount of blowing increases the MnO<sub>2</sub>; and nothing is left but running off the batch and using it up in the stills, where it takes very much acid and yields very little chlorine. The fact is that, in the absence of lime or other soluble protoxide, Mn(OH)<sub>2</sub> treated with air in



the wet way, at a temperature of  $60^{\circ}$  or so, oxidizes only to  $Mn_2O_3$ , which is the most stable of all the oxides of manganese, and is incapable of absorbing more oxygen in the wet way.

*Stiff batches* mostly occur under opposite conditions, viz., when the blast is not strong enough, but sometimes under unknown and unexplained circumstances. A stiff batch is known by the fact that the blowing-engine all at once commences to labour very heavily, the pressure indicated by the gauge on the air-vessel increases rapidly, and at last the engine stops entirely. This rarely happens, except at the commencement of an operation—apparently when too much lime has been added, more than can combine with or replace the manganese, or more than the force of the blast can manage. In this case peculiar crystalline compounds are formed, which produce a thickening, or even a complete solidification of the mass. This happens more frequently with still-liquor from native manganese, on starting the process, when more lime is needed; for this reason the *second* addition of lime in this case ought to be made by instalments, which with liquors from recovered manganese is neither necessary nor advisable. A further cause of stiff batches is, heating the manganese liquor too much before adding the lime. It once happened to myself when the liquor had, by mistake, been got up to  $77^{\circ}C$ .  $55^{\circ}C$ . are sufficient; and  $65^{\circ}C$ . ought never to be surpassed. The temperature always rises a few degrees during the blowing, in consequence of the oxidation, in spite of the considerable cooling by the air blown in. The appearance of a stiff batch is that of lime slaked to a pasty condition only. Sometimes the whole operation must be interrupted, the stiff mass dug out of the oxidizer, and dissolved out of the pipes with acid. But it very rarely goes so far as that; this seems to have happened only at first, before it was known what has to be done when a batch gets stiff. The only remedy is, putting all available steam upon the blowing-engine, and at the same time running fresh manganese liquor into the oxidizer to dissolve the excess of lime, till the engine works again quite freely. As a rule such a batch will not come out very good at the last; it mostly shows a very high base (1 equivalent and upwards) and low  $MnO_2$  (something like 1.3 lb. per cubic foot), and settles very badly, if at all. With a sufficiently strong blowing-engine and proper treatment with lime, stiff batches do not occur at all. Frequently, however, especially with not entirely settled liquors and too slow working

of the blowing-engine, the contents of the oxidizer *froth up* so as to overflow at the top; the only and certain remedy here too is, starting the engine at full force.

The opinion of Post, that stiff batches are caused by a cementing action of calcium oxychloride on the solid particles, is decidedly wrong. Our table, p. 350, shows that solid oxychloride is only precipitated at such high concentrations of the  $\text{CaCl}_2$ , as never occur in practical work (20 to 30 per cent.); and Post's explanation is all the more irrational, as stiff batches only occur when the  $\text{CaCl}_2$  is *deficient*. It is positively refuted by the analysis of a stiff batch obtained in our experiments, quoted p. 350 *et seq.*, which showed that the filtrate contained much less  $\text{CaO}$  than corresponds to the  $\text{CaCl}_2$ , so that some  $\text{CaO}$  must have entered into combination with  $\text{MnO}$ ; also by other stiff batches, purposely produced, where the dry residue, freed from the filtrate by a vacuum-pump, contained 30.12 per cent.  $\text{CaO}$ , 14.11  $\text{MnO}_2$ , 41.32 total Mn, and only 0.83 Cl. There was more than enough  $\text{CaO}$  present to form a basic manganate,  $3 \text{CaO}, \text{MnO}_2$ , and more than 1 mol.  $\text{CaO}$  to 1 at. of total Mn. The existence of solid calcium oxychloride was thereby distinctly refuted.

Wiernik (Zsch. f. angew. Ch. 1894, p. 261) showed that stiff batches are caused either by too high temperatures or by a deficiency of  $\text{CaCl}_2$  in the liquors, viz. if these contain less than 2.4 or 2.5 mols.  $\text{CaCl}_2$  to 1 Mn, and if in that case more than 1.2 mol.  $\text{CaO}$  is employed for precipitation. But even then the risk of stiff batches exists only at a certain critical period, viz., as soon as the mixture in the oxidizing tower has reached 30 to 35 per cent., or better 36 to 39 per cent.  $\text{MnO}_2$ , and the quantity of 17 to 19 grms.  $\text{MnO}_2$  per litre. As soon as 25 to 30 grms.  $\text{MnO}_2$  per litre are present, corresponding to 55 to 65 per cent.  $\text{MnO}_2$ , the conditions for forming a stiff batch no longer exist; the mixture remains in the thin state, and the mud settles normally. By very strong blowing the danger of a stiff batch can be warded off, all the more as in that case the oxidation quickly goes beyond the critical point. Concerning the nature of the "cementing substance," Wiernik's analyses, like mine, refute Post's opinion; he believes that the thickening of the mass is probably caused by a certain proportion between  $\text{MnO}_2$  and  $\text{Mn}(\text{OH})_2$ , perhaps according to the formula  $2\text{MnO}, 1\text{MnO}_2, 2\text{CaO}$ ; but this cannot be established as certain, as the analysis meets with almost insurmountable difficulties.

Iezler's analyses of Weldon mud (Dingl. Journ. ccxxxix. p. 74) are useless, since his samples were very abnormally composed.

Twynam (Engl. pat. 4397, 1881) proposes decomposing the manganese liquors with dolomite, and then precipitating and recovering the magnesia by milk of lime. His process is very obscurely described, and is at all events impracticable.

*Treatment of the Concentrated Weldon Mud.*—Some works have an intermediate vessel between the mud-settlers and the chlorine-stills, in which a mechanical agitator rotates and makes the mud run more freely. This arrangement is unnecessary with good mud and a moderate distance from the stills; it is then sufficient to rake up the mud in the settlers themselves with wooden rakes. At other works they interpose a pan for heating up the mud before it enters the oxidizer; this saves time, steam, and dilution, but is very troublesome, and consequently very rarely done. At some factories they treat the mud, in special agitating-tubs, with dilute hydrochloric acid before running it into the stills, partly in order to remove the  $\text{CO}_2$ , which has been introduced by badly burnt lime, partly to lessen the base; but this complication of the process easily leads to a loss of chlorine, and consequently is not employed at most of the works.

We shall now describe the *treatment of the recovered manganese mud in the stills*. First, hydrochloric acid is run into the still to a depth of 2 feet—the hotter from the condensers the better; and then manganese mud is run into the sluice-valves, but not sufficient to generate too strong a current of chlorine, which would blow the water out of the hydraulic lutes. With a little attention a perfectly even current of gas can be produced. The manganese-mud is run in till the dark colour of the liquid taken out of the test-cock shows that there is enough of it; steam is then blown in (frequently already before this stage), whereupon the liquor again clears up if acid be present. The limit is reached when at a sufficient temperature the liquid is clear but coffee-coloured (a light yellow colour showing an excess of acid) and, poured upon chalk, does not produce *strong* effervescence. It is of course preferable to test directly for free acid; this is best done by running in caustic soda from a burette till a permanent precipitate begins to appear (pp. 279 & 306):  $\frac{1}{2}$  per cent. of free acid is normal, 1 per cent. more than necessary, but as much as this is found even at well-conducted works. But the saturation of the acid ought not to go too far; for then un-

doubtedly some manganese mud would remain behind undissolved, subside along with the neutralizing mud, and be lost. When the proper point has been reached, the contents of the still are run into the lower-situated neutralizing well, and the whole cycle of operations begins anew. Each operation in the stills lasts from 4 to 6 hours.

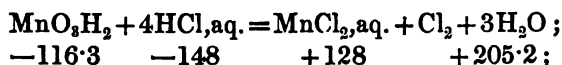
It should not be overlooked that 1 per cent. HCl in Weldon still-liquor means a great deal more than in liquor from native manganese ore. In the Weldon stills the acid is not merely diluted by the steam blown in, as in the old stills, but much more by the  $\text{CaCl}_2$  solution introduced with the recovered mud, up to such a degree that in the end about  $3\frac{1}{2}$  vols. of still-liquor are present to 1 vol. hydrochloric acid employed. If the latter showed 30 per cent. HCl, and the still-liquor 1 per cent., in reality only 26.5 per cent. HCl had been utilized, and 3.5 per cent. have been left free and must be afterwards neutralized by limestone-dust (p. 338). At most English works formerly the acid employed tested much less than 30 per cent., so that  $\frac{1}{3}$  or  $\frac{1}{2}$  of the HCl was lost in the still-liquor, of which loss very few manufacturers were aware.

Under these circumstances there was a very good reason for the endeavours not to neutralize that free acid by limestone, but by fresh Weldon mud, and thus to turn it to good use (p. 340). This, as we have seen, cannot be done when working with hydrochloric acid containing sulphuric acid, and even when the latter had been removed the process did not seem sufficiently remunerative to most manufacturers (probably owing to the just-mentioned oversight), so that very few of them made up their mind to carry that very rational process into practice. But we have seen on p. 341 that this matter is now better understood, and the above process has become general.

At a large English factory the following special *Rules for Bleaching-powder Men* have been drawn up, which are recommended by the 22nd Alkali Inspectors' Report, p. 54:—1. Manganese mud must not be run into a chlorine-still at such a speed as will cause chlorine to escape out of any lute on a main or through any joint of a pipe. 2. A still must not be run or emptied until all the chlorine generated in the still has, so far as may be practicable, been worked off. 3. Every lute in connexion with any pipe which conveys chlorine must be examined at least twice in every 24

hours; that is, at least once between 6 and 8 A.M. and once between 5 and 7 P.M. 4. When the supply of chlorine exceeds what is requisite, the main must be immediately disconnected, or the working of chlorine in the stills must be slackened. 5. The lutes on the bleaching-powder chambers are only to be opened in the presence of the foremen, and the doors are only to be opened at daylight in the presence of the manager, after the chambers have been tested. 6. Every defect that may cause an escape of chlorine or acid gas, or any leakage of gas or liquor, or any irregularity in any process, must be at once reported to the foreman. 7. Every bleaching-powder man who violates any of the foregoing rules will be liable to a fine of five shillings for every such violation.

The *thermochemical data* for the Weldon process are given by Fischer (*Zschr. f. ang. Chem.* 1888, p. 549) as follows:—In the transition from manganous hydrate,  $\text{Mn}(\text{OH})_2$ , to hydrated peroxide,  $\text{MnO}_2\text{H}_2$ , there is liberated for each gram-molecule  $116.3 - 94.8 = 21.5$  calories. The decomposition of the latter with hydrochloric acid yields:—



that is, an excess of 70 calories. Hence the reaction proceeds easily, as soon as the necessary temperature has been once attained. [This calculation suffers from the fault that Weldon mud is not  $\text{MnO}_2\text{H}_2$ , but a mixture of  $2(\text{MnO}_2)\text{CaO}$  with  $(\text{MnO}_2)\text{CaO}$ ; of these compounds we do not know the heat of formation.]

#### *Analytical Methods for the Weldon Process.*

The rough methods for testing the still-liquor and the contents of the oxidizer have been cited above (pp. 306 & 344): we must now explain the more accurate methods for testing the recovered mud for  $\text{MnO}_2$ , base, and total manganese. The reagents required are:—a strong filtered solution of bleach-liquor (not standardized); a solution of about 100 grams crystallized ferrous sulphate and 100 grams pure sulphuric acid per litre; a standard solution of potassium permanganate—most conveniently made from pure crystals, of seminormal strength, *i. e.* 1 cub. centim. corresponding to 0.004 gram oxygen or 0.02175 gram Mn, identical with that employed

in testing nitrous vitriol\*; a normal solution of oxalic acid (63 grams per litre); a normal solution of caustic soda (31 grams NaOH per litre).

In testing for  $\text{MnO}_2$ , 25 cub. cent. of the iron solution are pipetted into a beaker, diluted with cold water to 100 or 200 cub. cent., and standardized by the permanganate solution: this suffices for the whole day. Another 25 cub. cent. of the iron solution are treated with 10 cub. cent. of manganese mud. This is taken out of the well-shaken sample-bottle with a pipette, which is then washed outside; its contents are run into the iron solution, and the pipette rinsed out into the same by means of the washing-bottle. The beaker being shaken, the mud is dissolved in a few seconds; the liquid is then diluted, and titrated back with permanganate. The number of cub. cent. used, deducted from that used for the iron alone, corresponds to the  $\text{MnO}_2$ , and at once yields its quantity per litre on being multiplied by 2.175. If, as usual in England, it is preferred estimating the  $\text{MnO}_2$  in pounds per cubic foot, a pipette containing  $\frac{1}{2}$  or 1 cubic inch is employed, and the following formula serves for calculating the result (for one cubic inch):—

$$\text{MnO}_2 = \frac{0.02175 \times 1728}{453.5} x = 0.0830x;$$

where  $x$  means the number of cub. cent. of seminormal permanganate, found by subtracting those employed for retitrating from those employed in standardizing the iron solution. The number of pounds per cubic foot is found from the number expressing the grams per litre by multiplying the latter by 0.0624†.

The "base," as we know, comprises all constituents of the mud which neutralize acid, leaving behind pure  $\text{MnO}_2$ . The base may be lime, magnesia, or protoxide of manganese; the mutual propor-

\* This is more convenient for use than the potassium dichromate proposed by Weldon.

† The accuracy of the permanganate-iron test has been disputed by Post (Ber. deutsch. chem. Ges. xii. p. 1639). He obtained by Bunsen's iodine test results 10 per cent. lower than the above test indicated. But in very careful special comparative trials instituted by me the results of the permanganate, the bichromate, and the iodine test were found identical (Dingl. Journ. ccxxxv. p. 300). My experiments (as well as those on the testing of Weldon mud generally) are described in the Chem. News, vol. xli. p. 129.

tion of these bodies influences neither the analytical operation nor the consumption of acid in the chlorine-stills; hence, as a rule, only the total base is sought, in the following way:—Twenty-five cub. centims. of normal oxalic acid (with a very high base this is too little) are diluted to about 100 cub. cent., and heated to 60° or 80° C.; 10 cub. cent. of manganese mud are added, with the above-mentioned precaution of washing the pipette &c., and heat applied till the precipitate has become pure white, not cream-coloured—which usually takes less than one minute. Then it is retitrated with standard caustic soda, in order to learn the number of cubic centims. of oxalic acid consumed; the exact determination of the point of neutralization is not very easy, because litmus, even in excess, does not give a very sharp indication. (As an indicator, litmus or phenolphthalein must be used, not methyl-orange, on account of the oxalic acid.) Hence the statements of factory-chemists about their Weldon base are not always trustworthy. The object is attained much more accurately and not much more slowly if the whole is diluted to 202 cub. cent. (where 2 cub. cent. correspond to the bulk of the precipitate), passed through a dry filter, and 100 cub. cent. of the filtrate retitrated with caustic soda, when the indication, in the absence of a precipitate, is much sharper. The oxalic acid acts in this way: first it decomposes with all the  $\text{MnO}_2$  into  $\text{MnO}$  and  $\text{CO}_2$ ; consequently for each cub. cent. of seminormal permanganate,  $\frac{1}{2}$  cub. cent. of oxalic acid will be consumed for this object. Exactly the same quantity is consumed to form an oxalate with  $\text{MnO}$ ; and a further quantity is consumed for saturating any  $\text{MnO}$  present over and above that produced from  $\text{MnO}_2$ , as well as  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ , &c. The latter is the quantity sought for; and it is found by deducting from the number of cubic centims. of oxalic acid consumed that of the cubic centims. of permanganate found in titrating for  $\text{MnO}$ : the remainder is equal to the base; and the proportion to  $\text{MnO}$  is found by dividing this remainder by *half* the cub. cent. of permanganate (as this is seminormal and the oxalic acid normal).

Suppose the titre of the iron solution to have been found = 28.0 permanganate. After running in 10 cub. cent. of manganese mud, only 11.5 permanganate have been required; hence  $x = 16.5$ , and the strength of the mud = 35.88 grams per litre, or 2.24 lb. per cubic foot. 10 cub. cent. of mud are heated with 25 cub. cent. oxalic acid, diluted to 202 cub. cent.; 100 cub. cent. filtered

require 1·6 normal caustic. The difference between twice this and 25, = 21·8, gives the total oxalic acid consumed. Deducting from this 16·5 (the above  $x$ ) for  $\text{MnO}_2$ , leaves 5·3 for base. The proportion ( $\frac{1}{2} \times 16·5 =$ )  $8·25 : 5·3 = 1 : 0·642$  shows 0·642 to have been the base.

The total manganese in the mud is estimated only now and then, both because it takes a little more time and because it is not of such importance as the total base. It is, however, very interesting, and must be done from time to time. 10 cub. cent. of mud are boiled with  $\text{HCl}$  till all the chlorine is driven off, the free acid exactly neutralized by caustic soda, and the liquor again raised to the boiling-point; a clear filtered solution of bleaching-powder is added till the liquid shows a pink colour, from the formation of a trace of permanganate; this trace is again destroyed by adding a drop of alcohol. Now all the manganese is in the state of a precipitate of  $\text{MnO}_2$ ; this is thrown upon a filter, completely washed till the filtrate gives no more reaction with potassium iodide, the precipitate dissolved in the acidulated solution of ferrous sulphate, and retitrated by permanganate, precisely as in estimating the  $\text{MnO}_2$  existing as such in the mud.

Jurisch (Chem. Industrie, 1880, p. 193) describes some modification in the testing of Weldon mud, with complicated formulæ, seldom used by anybody else.

#### *Yields and Costs.*

The *yield of bleaching-powder* in the Weldon process is in England always stated in terms of the quantity of common salt decomposed for 20 cwt. of full-strength bleach. This result depends upon several circumstances: from the completeness of the condensation of  $\text{HCl}$  in the saltcake process; from the strength of the hydrochloric acid obtained in that process; from the utilization of  $\text{HCl}$  in the Weldon still; from the concentration of the Weldon mud (dilute mud causes too much dilution in the still); from the degree of oxidation and the base in the mud,—altogether from all the various stages of the process. Formerly a decomposition of 57 cwt. salt to a ton of bleach was considered as a good average, but frequently more than 60 cwt. of salt was consumed; with open roasters, even 70 or 80 cwt. The consumption of hydrochloric acid at that time was calculated as 4600 to 4800 litres of spec. grav. 1·12 = 1250 kil. real  $\text{HCl}$  to 1000 kil. of 37 per cent.



bleach; or else 4000 litres of spec. grav. 1.14, which comes to the same thing. In the bleaching-powder we find only the chlorine corresponding to 380 kil. HCl, that is a little over 30 per cent. of the total HCl employed. At Aussig they used in 1878  $3\frac{1}{2}$  tons acid of spec. grav. 1.17 to 1.18 to 1 ton of bleach=1155 kil. HCl to 1000 bleach, that is a little less than the above.

Since the still-liquor is no longer saturated with limestone dust but with Weldon mud itself (pp. 340 & 341), which utilizes the free acid, the yields are much better, and now average 44 cwt. salt to 20 cwt. bleach; but some works do even better than that.

Another matter requiring attention is the supply of *native manganese ore* to make up the loss of manganese liquor. In this respect also the various factories differ very much; but by more careful manipulation this loss has constantly decreased. Some factories, formerly losing 5 per cent., now lose only  $2\frac{1}{2}$  per cent., or even only  $1\frac{1}{2}$  per cent. manganese. With careless work as much as 10 per cent. may be lost. Apart from purely mechanical losses, attributable to downright slovenliness, care must be taken not to leave any more  $MnCl_2$  in the neutralizing mud than is absolutely unavoidable. The better the liquor is neutralized in the stills themselves by manganese mud, the less calcium carbonate will be necessary outside (comp. also pp. 338 & 339). Theoretically, for making one ton of 37-per-cent. bleach,  $9\frac{1}{4}$  cwt. of regenerated  $MnO_2$  are required; but practically, owing to the unavoidable loss of chlorine, about 10 cwt. are needed, which are contained in about 500 cubic feet of good manganese mud as it comes from the oxidizer.

Some practical men state that the chlorine from recovered manganese acts much more quickly upon the surface of the lime in the chambers than that from native manganese ore, and that consequently in the former case the depth of the layer cannot be made so great as in the latter; say in the proportion of  $8\frac{1}{2}$  to 10. Whether this is really the case, does not seem to be entirely proved. At one of the largest factories, for each ton of bleach per week to be made by Weldon's process 200 square feet of chamber-floor are assumed. In any case the bleach made by this process is of excellent quality, up to 39 per cent., and is said to lose less in the casks than that made by the old process (about  $\frac{1}{2}$  per cent. against  $1\frac{1}{2}$  per cent.).

The *cost of labour* in Weldon's process is not much greater on a

large than on a smaller scale, of course apart from the cost of preparing the lime and packing the bleach. There is always one man per shift needed for oxidizing (who can also undertake the general supervision), one man for making the milk of lime, one for the mud-settlers, one for the Weldon stills, one for the neutralizing-wells, one for the native-manganese stills, and one for the steam-boilers. With this staff the manganese may be recovered and chlorine generated for 15 tons of bleach per day; but even if only 5 tons be made, not much less labour will be required—only that employed in lime-slacking, wheeling of coals and cinders, &c., will be reduced. Usually the whole labour is let to a gang of men at so much per ton of bleach, at prices differing according to the size of the works.

*The cost of bleaching-powder by Weldon's process about the year 1875 can be seen from the following statement of results of working extending over a long period:—*

	£	s.	d.
Lime, 27 cwt., at 16s. per ton .....	1	1	7
Limestone, 5 cwt., at 10s. per ton.....	0	2	6
Coals, 25 cwt., at 12s. per ton .....	0	15	0
Manganese, 1 cwt., at 100s. per ton .....	0	5	0
Casks .....	1	0	0
Wages .....	0	10	0

Cost of 1 ton 37-per-cent. bleach...£3 14 1  
(without general expenses).

The following is another authentic cost-account (of 1874, when materials were still very costly), from a works at St. Helens:—

15½ cwt. coals, at 9s. ....	0	6	10½
11¾ cwt. lime for oxidizer, at 18s. 6d. ...	0	9	10½
11½ cwt. lime for powder, at 20s. ....	0	11	6
6½ cwt. limestone dust, at 10s.....	0	3	3
1½ cwt. manganese, at 130s.....	0	8	1½
Wages (including boilermen and bleach- ing-powder) .....	} 0	17	8½
Casks .....			
		0	17 1
		£3	14 5

Cost, inclusive of general expenses, Liverpool commission, &c.,  
f.o. b. £6 5s. 0d. (at that period).

The cost of recovering as much manganese as suffices for producing 60 tons of strong bleach per week was stated in 1870, by a large Widnes works, at :—

	£	s.	d.
60 tons lime, at 12 <i>s.</i> .....	36	0	0
Slaking and sifting the same.....	6	0	0
12 tons limestone, at 8 <i>s.</i> 6 <i>d.</i> .....	5	2	0
Steam .....	12	10	0
Wages for engine and oxidizing.....	2	16	0
Wages for neutralizing and pumping the manganese liquor .....	1	19	0
Wages for making and pumping milk of lime .....			
	3	0	0
	<hr/>		
	£67	7	0
Deduct 2 <i>s.</i> per ton saving in labour on making the bleach.....	6	0	0
	<hr/>		
	£61	7	0

This is £1 0s. 6d. per ton of 37-per-cent. bleach, exclusive of interest, management, and repairs. But at that time one-third too much lime was used; and the cost of sifting it has been entirely saved, so that now the cost of recovery is only 15s. 6d. exclusive, or 20s. inclusive of interest &c. per ton of bleach.

At Dieuze in 1878 (private information) the following quantities of substance were required for 100 kilog. of bleach 108° Gay-Lussac :—

Manganese (58 per cent.) .....	2.9 kilog.
Hydrochloric acid, 32° Tw.....	397 „
Lime for the chambers .....	60 „
Lime for the oxidizers .....	65 „
Limestone for neutralizing .....	16 „

The consumption of coals, on an average of all works (communication from Mr. Weldon 1878), amounts to 16 cwt. per ton of 38-per-cent. bleach; but one works in France manages with 9 cwt. In neither case is the burning of the lime included.

The Chemical Trade Journal, vi. p. 15, gives the following statement of the cost of producing one ton of 36-per-cent. bleach by the Weldon process in 1890 :—

	£	s.	d.
Coals.....	0	6	0
Lime .....	0	14	0
Limestone dust .....	0	1	0
Manganese ore .....	0	4	2
Wages .....	0	13	4
Casks .....	0	13	0
Depreciation 10 per cent. ....	0	5	0
Repairs.....	0	4	3
General expenses.....	0	6	8
4 tons hydrochloric acid.....	2	0	0
	<hr/>		
	£5	7	5

Cost of plant for making 100 tons bleach per week by the Weldon process = £12,000.

A calculation given by Davis (Journ. Soc. Chem. Ind. 1883, p. 155) does not include hydrochloric acid, wear and tear, and general expenses:—

	£	s.	d.
Coals .....	0	4	6
Lime for oxidizing .....	0	10	8
„ bleach .....	0	10	8
Limestone dust .....	0	2	2
Manganese ore.....	0	3	0
Wages .....	0	15	0
Casks .....	0	17	0
	<hr/>		
	£3	3	0

The following is an authentic cost-sheet of a Continental works for the years 1891–92, showing the cost of making 100 kilog. bleaching-powder of 100° Gay-Lussac (=31·8 per cent. available chlorine):—

	Kil.	@ frs.	Frs.
Hydrochloric acid, spec. gr. 1·16 ...	404·2	21·50	8·68
Manganese ore .....	6·4	70·00	0·45
Lime .....	103	38·80	3·48
Limestone .....	23·8	6·00	0·14
Coals .....	117	17·00	1·98
Wages .....	...	...	1·16
Repairs.....	...	...	1·20
General expenses.....	...	...	0·50
Packages and loading .....	...	...	1·50
			<hr/>
			19·09

*Other uses of Weldon Mud.*

In consequence of the extremely fine division of Weldon mud, its action is much more energetic than that of natural manganese ore, not merely on hydrochloric acid, but also in other cases; it even produces reactions quite impossible with the native ore. In some cases this may be caused by the fact that Weldon mud does not consist of anhydrous  $\text{MnO}_2$ , but either of the hydrate of manganous acid,  $\text{MnO}_2\text{H}_2$ , or of salts of this with calcium and other metals. Its almost complete freedom from iron is sometimes a very important advantage over the natural ore, *e. g.* in the manufacture of glass, where, however, as in many other cases, the high price of recovered manganese dioxide rarely admits of its employment.

A very important use of Weldon mud is that for purifying aluminium sulphate from iron, by Kynaston's process (Engl. pat. 3809, 1882; comp. Journ. Soc. Chem. Ind. 1886, p. 20), which has been proved to be the best of all processes for that object.

Hood and Salamon (Dingl. Journ. cclxviii. p. 136) have proposed Weldon mud for purifying coal-gas, which comes to the same as the application of mud containing manganese for desulphurizing the liquid from old Leblanc-waste heaps (p. 340).

*Waste Calcium-Chloride Liquor.*

For the *calcium chloride* which is obtained in such enormous quantity in the Weldon process, no use has hitherto been found to any considerable extent. As it is quite free from iron, it can be obtained by evaporation and fusing as a perfectly white mass similar to caustic soda, and, like this, is packed in sheet-iron drums. It is employed at alizarine-works, at some sugar-works as an addition in saturating, for making barium chloride from barium sulphate and coal (p. 315), for making pearl-hardening (Vol. II. p. 721); but most of the  $\text{CaCl}_2$  solution runs away to waste. It is quite harmless in a sanitary respect, but renders the water hard. It has been proposed (*e. g.* by Hargreaves, Chem. News, xvi. p. 131) as an addition to manures in order to precipitate the phosphoric acid and keep it from being washed away, also as an antifermenting and antiseptic substance which at the same time fixes the more volatile ammonia compounds as chloride. The dark brown liquors from boiling esparto or wood-pulp, if on

account of the expense of fuel they cannot be worked for recovering the soda, at least can be deprived of nearly all organic substances by precipitation with  $\text{CaCl}_2$ ; and the resulting liquor, containing much  $\text{NaCl}$ , but very little coloured, can be run into watercourses without any fear.

Campbell and Boyd (Engl. pat. 5571, 1890) repeat the old proposal to add sulphate of soda to the waste liquor, in order to produce pearl-hardening and sodium chloride.

#### *Statistics.*

In 1877 there were 50 Weldon plants at work in England, Scotland, and Ireland, turning out about 105,000 tons of bleaching-powder or its equivalent in chlorate of potash. This is about 90 per cent. of all that was then manufactured in Great Britain. The quantity of bleaching-powder and chlorate of potash made by the Weldon process at the present time must be considerably greater than in 1877, but statistical information on this point is not obtainable. In France there were 8 plants, turning out 20,000 tons of bleach and chlorate, being all that was made in that country; in Germany 7 or 8, Austria 2, Norway 1, Belgium 1. Most of the bleaching-powder produced was then, and probably is even now, manufactured by that process.

## CHAPTER XVIII.

## THE DEACON PROCESS.

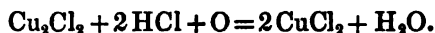
THE decomposition of hydrochloric acid by atmospheric air was first patented by Oxland in 1845 (No. 10528). The mixture of both gases is passed through red-hot pumice; the gas leaving the apparatus is cooled, and the undecomposed HCl is washed out by water. Further patents in this direction will be mentioned in the last Chapter of this book.

The yield of chlorine in Oxland's or any other process by which chlorine is made from hydrogen chloride and air by mere heating, even in the presence of porous substances, is extremely small, and such processes have no practical value.

This problem was again dealt with in another way, viz. by the employment of the *chlorides of copper*. Vogel (Dingl. Journ. cxxxvi. p. 237) in 1855 proposed evolving chlorine from cupric chloride by heating it to an incipient red heat :



The cuprous chloride is mixed with hydrochloric acid, and, by the atmospheric oxygen, converted first into oxychloride ( $\text{CuCl}_2, 3\text{CuO}, 3\text{H}_2\text{O}$ ) and then again into cupric chloride. The final stage is represented by the reaction :



But on working on a large scale not half, but only one third of the chlorine of  $\text{CuCl}_2$  is said to be obtained, viz. 13·8 per cent. of the cupric chloride. According to Hofmann's Report by the Juries, 1862, p. 35, Gatty examined the above proposal, and found that the chlorides of copper quickly corrode stoneware vessels and the hardest fire-bricks, so that hardly any vessels can be made for evaporating and calcining them. This manipulation is very dangerous to health; and even a small loss of copper, considering its high price, would make the process economically impossible.

Laurent patented exactly the same process as novel (No. 163, 1860). Cupric chloride is made by dissolving  $\text{CuO}$  in  $\text{HCl}$ , or  $\text{Cu}$  in aqua regia, or precipitating a solution of  $\text{CuSO}_4$  by  $\text{BaCl}_2$  or  $\text{CaCl}_2$ . The solution is dried down and heated at  $100^\circ$  or  $150^\circ \text{C}$ . till the water is given off and a brownish-yellow powder remains; this is mixed with half its weight of sand, and kept heated in a retort to  $220^\circ$  or  $300^\circ \text{C}$ . till half of the chlorine contained in the cupric chloride has been driven off. The remaining mixture of cuprous chloride and sand is mixed with hydrochloric acid and evaporated in a current of air; hydrated cupric chloride is obtained by crystallization, and heated with or without sand in order to drive off the water and begin the process anew. This process possesses a certain importance, because it may be considered one of the precursors of Deacon's process. As No. 5, 1864, Trégomain patented the same process with unimportant modifications: he fuses the cupric chloride, grinds it, converts it into oxychloride in a current of air, treats this with liquid or gaseous  $\text{HCl}$ , and obtains the  $\text{CuCl}_2$  formed by lixiviation and crystallization.

A new patent was taken by Mallet (No. 3171, 1866) for converting cuprous chloride by oxygen into oxychloride, which gives off its oxygen at a dark-red heat and is again converted into cuprous chloride. He employs horizontal cylindrical cast-iron retorts, lined with an enamel not acted upon by the chlorides of copper, *e. g.* copper borate, silicate, or phosphate. The retorts have a discharging-aperture at the bottom; and in the elongation of their axis there is an exit-tube; they are placed in a furnace on rollers, which permit their rotation round their axis. The oxychloride is mixed with 15 to 20 per cent. of inert material, such as china-clay, sand, porcelain, or powdered fire-bricks; and the mixture always remains within the retort when in regular working. When oxygen alone is required, only a dark-red heat is applied. When gas has ceased to be evolved the retorts are cooled down and jets of steam and air directed into them while they are rotating, so that in two or three hours the oxychloride is regenerated. If, however,  $\text{HCl}$  gas is injected from the first, or if to the oxychloride formed at first  $\text{HCl}$  is added, cupric chloride is produced, from which chlorine can be obtained by heating. 100 kilog. of  $\text{CuCl}_2$  are stated to yield 6 or 7 cubic metres of chlorine gas; and as in 24 hours at least 4 or



5 operations can be performed, the above quantity suffices for a daily production of from 4 to 6 cwt. of bleaching-powder.

As long as the copper processes were carried out in the manner hitherto described they could not be technically successful, owing to the unavoidable large quantity of copper employed and the corresponding loss of copper. Success was only reached when Henry Deacon had conceived the notion of combining the ideas of Oxland and Vogel, by passing the mixture of air and hydrogen chloride, not over an indifferent substance like pumice, but over a porous substance impregnated with copper, and by turning the reaction into a *continuous* process, in which the successive reactions of the copper chlorides with HCl and O pass on within those porous substances. His first patent dates from April 29, 1868 (No. 1403); further 20 patents were taken out within the few years up to his death, which occurred in 1876. Deacon has himself publicly recognized the important services rendered in the working-out of his process by Ferdinand Hurter and by Eustace Carey.

Even now in England the remark is sometimes made that no German patent has been granted for the Deacon process (no more than for the Weldon process), and this is styled a designed "robbery." This reproach is not merely unjust, but simply ridiculous. Up to 1876 there was no patent law in existence for all Germany. An inventor would have had to apply for patents in the 36 single German States, many of which did not grant any patents at all. Prussia did grant patents, but merely for inventions embracing an entirely new principle (which could not be said of either Weldon's or Deacon's process); such inventions are, of course, very rare, and in fact only from 20 to 50 patents per annum were then granted in Prussia, which were mostly of little use to their owners, as the same invention could be worked in the adjoining small States without any patent. The injustice of the above reproach is all the more flagrant, since the Germans have not, as might be inferred therefrom, greedily thrown themselves upon the Deacon process. Only *two* factories have introduced it, and this was, at least in one case (if not in both), done on the strength of an understanding with the English patentees!

If the present German patent law (dating from 1876) had been in force at that period, there is no doubt whatever that Deacon would have obtained a patent, and that consequently the German

industry would have availed itself far more of his invention than was actually done, as the royalty would have assured a communication of the inventor's special experiences and an undisturbed use of the same.

Deacon's process became first more widely known in 1870 by a paper read by Mr. Deacon at the Liverpool Meeting of the British Association, which at once excited general attention and great expectations. That paper was reprinted in the 'Chemical News,' vol. xxii. p. 157. It starts from the fact, known long before, that a mixture of hydrochloric-acid gas and oxygen at a sufficient heat, especially on passing over red-hot porous materials, is partially split up with formation of chlorine and water :



but by the employment of certain substances, over which the mixture is passed, the decomposition was stated to take place at a lower temperature, and so completely that *all* the HCl could be decomposed and its chlorine liberated [this is both theoretically and practically wrong]. For this object a substance must be chosen which remains unchanged when the mixed gases pass over it, but influences the changes in the gases. Copper-salts possess this power in a very marked degree; and of these the sulphate is the most convenient. If pieces of common red brick are dipped into a solution of cupric sulphate and dried, charged into tubes, and the heated gases passed through, the reaction already sets in at 204° C., and is most active between 373° and 400°; at 427° C. cupric chloride begins to volatilize. Thus an indefinitely small particle of cupric sulphate can effect the liberation of the whole of the chlorine from an indefinitely large mass of hydrochloric acid gas. The activity of the cupric sulphate seems to depend entirely upon its surface. According to the speed of the current of gas more or less HCl is decomposed; but the quantity of chlorine liberated is a constant for the same apparatus, temperature, and time. Even the admixture of indifferent gases, as aqueous vapour, nitrogen, carbonic acid, sulphuric acid, does not change the law. Deacon was led to this observation by theoretical deductions from the previously discovered process of preparing chlorine by heating cupric chloride, oxidizing the cuprous chloride, adding HCl, and again liberating chlorine from the product formed. But his idea

differs from this in the important point that he carries on the reactions not successively, but simultaneously, and thus arrives at a continuous process of preparing chlorine. He further found the chlorine gas, diluted with so much nitrogen, to yield strong bleaching-powder if passed over a large surface of lime in such a manner that the strongest gas meets with the most nearly saturated, the weakest gas with fresh lime. Deacon states the reaction itself to be a source of heat, 4 volumes of  $\text{HCl}$  and 1 of  $\text{O}$  (*i. e.* 5 volumes) yielding 2 vols.  $\text{H}_2\text{O}$  and 2 vols.  $\text{Cl}$  = 4 volumes. If from the 34,462 units of heat, resulting from the union of oxygen and hydrogen, the 23,783 units are deducted which are required as the combining-heat of chlorine and hydrogen, an excess of 10,679 units of heat remains to be given out. The water and nitrogen present absorb this heat and reduce the apparent temperature; but this evolution of heat is a material assistance in making up for the loss of heat in the decomposing-apparatus by radiation. [Upon this point a discussion afterwards arose: Thomsen (*Dingl. Journ.* xcix. p. 128) charged Deacon with having overlooked that the water formed is not in a liquid but in a gaseous form, which reduces the heat to be disposed of to one half; Hurter replied in the '*Berichte der deutschen chemischen Gesellschaft*,' 1871, p. 199; and Thomsen, *ib.* p. 596, upheld his first position.]

Deacon further states that, in the gases evolved in the ordinary salt-decomposing apparatus, sufficient air is present to liberate all the chlorine; the heat of the gas requires to be carefully regulated, but can be easily kept constant by means of a brickwork regulator and an improved pyrometer. Iron resists the action of chlorine gas very well [but only in the perfectly *dry* state!]; the large bulk of the gases causes no difficulty; and the only real, but not very important difficulty is the volatilization of some ferric chloride, which is deposited in the bricks saturated with copper-salt, and must be kept out by a purifying apparatus specially interposed.

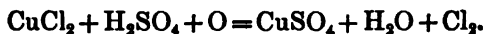
Even after the first difficulties appeared to be overcome, Deacon incessantly made new endeavours to clear up the conditions of the process; their results are stated in a lecture delivered before the London Chemical Society (*Chem. Soc. Journ.* x. pp. 725-767). The following is a brief abstract of them :—

Only such substances exert a "catalytic" action upon a mixture of HCl gas and air as are chemically acted upon by hydrochloric acid, especially those which form chlorides with it decomposable by hot dry air with evolution of chlorine; but the amount of action of the HCl upon those substances is not proportional to the amount of chlorine obtained by continuous action. It is indefinitely small with clays, most pumice stones, ferric and chromic oxides. To obtain the action in the highest degree, the substance must at the same time possess affinity for oxygen at the temperature worked with. The most active substances are the salts of copper—of which the sulphate is always employed, on account of its cheapness. There is always some cupric chloride formed, but fortunately not in sensible quantities, except at a temperature above the most favourable to the evolution of chlorine. Not the mass, but the surface of the copper-salt determines the amount of the reaction. For the same mixtures of HCl and O, and at the same temperatures, the quantity of HCl decomposed by a molecule of a copper-salt in a given time depends upon the number of times the molecules of the gaseous mixture are passed through the sphere of action of the copper-salt. Inversely the activity of a molecule of copper-salt depends upon the speed with which fresh matter is presented to, and the products are removed from it. In this no force is created, but (as Bunsen says in his 'Gasometry,' Engl. transl. p. 255) "catalytic action is not an equivalent to the unlimited amount of labour; but for every decomposition effected an equivalent amount of force is absorbed, just as, in the case of a weight raised by a falling body, a force is expended exactly equivalent to the work done." In long parallel tubes of the same diameter, the number of opportunities of action in the same time is nearly the same at all velocities of the current of gas; in similar tubes of different diameters it remains the same when the velocities of the currents of gas are in inverse proportion to the squares of the tubes' diameters. In porous masses the opportunities of action increase with increased velocities of the current of gas in nearly direct proportion. Other conditions remaining the same, the percentage of hydrochloric acid decomposed in any given time varies with the square root of the proportional volume of oxygen to hydrochloric acid. The cupric chloride formed bears no definite proportion to the quantity of chlorine evolved. As the sphere of action includes

molecules not in contact with the copper-salt, therefore HCl must be decomposed under circumstances where the union of either element with the copper-salt is impossible; *i. e.* the decomposition must be in part, if not entirely, caused by the resultant of the forces engaged, and therefore direct from  $2\text{HCl} + \text{O}$  to  $\text{H}_2\text{O} + \text{Cl}$ .

If the truth must be told, the somewhat pretentious theoretical investigations of Deacon, so far as can be seen, have had next to no influence in promoting the practical working-out of the process; the latter has had to be done according to the ordinary homely technical rules. If Deacon had only not been so positively convinced that he had already discovered the true theory of the process called after him, even to the oscillations of the molecules, there would not have been so many and such costly mistakes made by himself and others, instead of proceeding cautiously with further investigations (Hasenclever, *Dingl. Journ.* ccxxii. p. 257).

A further contribution to the theory of the Deacon process has been made by Hensgen (*Dingl. Journ.* ccxxvii. p. 369). He starts from his observations on the decomposition of anhydrous cupric sulphate by dry HCl gas (Vol. II. p. 40), and finds that, in the case of simultaneous action of oxygen, the decomposition takes place almost quantitatively according to the equation



When air was employed instead of oxygen, the decomposition was less complete. Such a mixture of  $\text{CuCl}_2$  and  $\text{H}_2\text{SO}_4$  is just formed by the action of HCl upon anhydrous cupric sulphate. But when more sulphuric acid is present than is required by the above equation, the HCl is given off so quickly that the oxygen as it arrives has scarcely time to act, and thus but little chlorine is produced. The reactions which take place when HCl and air act upon  $\text{CuCl}_2$  without sulphuric acid, are represented by Hensgen in this way:—

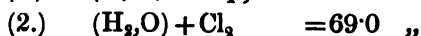
1.  $6\text{CuCl}_2 = 2(\text{CuCl}_2 + \text{Cu}_2\text{Cl}_2) + 4\text{Cl}$ ;
2.  $2(\text{CuCl}_2 + \text{Cu}_2\text{Cl}_2) = 3\text{Cu}_2\text{Cl}_2 + 2\text{Cl}$ ;
3.  $\text{Cu}_2\text{Cl}_2 + \text{O} = \text{CuO}, \text{CuCl}_2$ ;
4.  $\text{CuO}, \text{CuCl}_2 + 2\text{HCl} = 2\text{CuCl}_2 + \text{H}_2\text{O}$ .

The following simpler formulæ will suffice for our purpose:—

1.  $2\text{CuCl}_2 = \text{Cu}_2\text{Cl}_2 + \text{Cl}_2$ ;
2.  $\text{Cu}_2\text{Cl}_2 + \text{O}_2 = 2\text{CuO} + \text{Cl}_2$ ;
3.  $2\text{CuO} + 4\text{HCl} = 2\text{CuCl}_2 + 2\text{H}_2\text{O}$ .

Experimental investigations on the equilibrium between HCl, O, Cl, and H<sub>2</sub>O have been made by Hautefeuille and Margottet (Compt. Rend. cix. p. 641) and Le Châtelier (*ead. loco*, p. 664), both reproduced in Journ. Soc. Chem. Ind. 1889, pp. 184 & 185; but these do not possess any immediate practical importance for the Deacon process.

The thermal phenomena in the Deacon process are as follows :—  
If oxygen acts on *liquid* hydrochloric acid, no decomposition takes place. The formation heats are :—



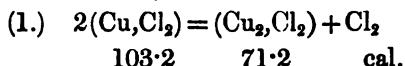
Hence 9·8 cal. must be introduced from without in order to get from system No. 1 to No. 2, and this can be done directly only by electrical energy (or light &c.), or indirectly by oxygen carriers, such as manganese peroxide, chromates, &c.

It is different in the *gaseous* state. Here we have :—



Hence in the transition from No. 1 to No. 2, 14·2 calories are set free, and this transition can take place without any importation of energy from without; it is even a source of heat, although not to the extent asserted by Deacon (p. 375).

In spite of this, the above transition cannot be carried out to any considerable extent unless it is assisted by a carrier of the reaction (a "catalytic" or "contact" substance), for which purpose only the oxides of copper are practicable. Cupric chloride, CuCl<sub>2</sub>, is dissociated by heating; at a temperature of about 400° C. it splits up into protochloride and free chlorine, with the following heat phenomena (in the solid state) :—

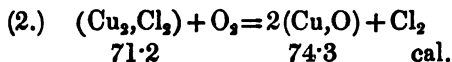


The 32 calories required for the transition are furnished by the heating to 400° C.\*

Cuprous chloride has the property of easily absorbing oxygen

\* This is a fresh proof of the uncertainty of all predictions founded on thermochemical data (comp. Vol. II. p. 477, *inter alia*). By the reaction  $2\text{HCl} + \text{O} = \text{H}_2\text{O} + \text{Cl}_2$ , without employing a special "carrier," or "contact-substance," much heat is liberated; and this reaction should therefore proceed very easily, whereas the direct contrary is the case. On the other hand,

at ordinary temperatures, with formation of an oxychloride; at high temperatures it yields in contact with oxygen directly cupric oxide and chlorine:—



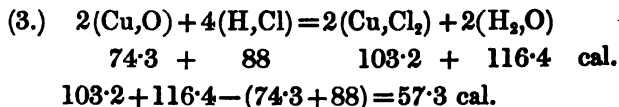
according to the general style of arguing from thermochemical data, the reaction  $2\text{CuCl}_2 = \text{Cu}_2\text{Cl}_2 + \text{Cl}_2$  should set in with great difficulty and very incompletely even at a very high temperature, whereas, again, the exact contrary takes place. Hurter endeavours to explain this contradiction by the following statement (Journ. Soc. Chem. Inst. 1883, p. 107):—"The action of copper in this process is almost unique, and depends upon the property of cupric chloride of becoming capable of dissociation—to be, so to say, able to convert heat into chemical energy." In plain English this means:—precisely in one of the most important reactions of the case which was to be explained, viz. the Deacon process, treated by Deacon and by Hurter himself with such an expenditure of arguments taken from scientific considerations, the aid of thermochemistry, to which they constantly appeal, entirely *fails*, and refuge is taken in the assumption of an "almost unique" property of copper. But this property itself remains unexplained. So far from it being an almost unique property of cupric chloride to convert heat into chemical energy, precisely the same property belongs, *e.g.*, to sulphuric acid, to sulphuric anhydride, to carbonic anhydride—all of which are dissociated by mere heating—besides many other substances; and another long series of examples of converting heat into chemical energy is furnished by the reduction of the metallic oxides by carbon, and, among others, by the Leblanc process itself, in which a principal part is played by the endothermic reduction of sodium sulphate to sulphide (Vol. II. p. 477).

Under these circumstances I do not see the utility of giving more details of Hurter's reasoning, or illustrating his graphical delineation of thermochemical data, to which particular value is attributed by some writers, since they leave us unenlightened in the very case for which they are invoked. On the contrary, I cannot but look at such "scientific treatment" of technical questions, with its mathematical apparatus, as possessing a very restricted value and sometimes leading to real delusions; the essence of the phenomena is *not* elucidated thereby; nor is there any proof given of its practical utility. If Deacon really *had* acted upon those alleged scientific premises, they would have prevented him from pursuing his invention, as the dissociation of  $\text{CuCl}_2$  is contrary to the usual thermochemical reasoning.

The logical fault committed by this kind of argument is that it takes account of only one side of a very complicated series of conditions and phenomena, viz., that which is sufficiently adapted for exact treatment; but the net result may be more influenced by other sides of the problem, hitherto inaccessible to such treatment.

It is unnecessary to say that nothing is further from my mind than to depreciate a really scientific discussion of technical processes; but I feel bound to protest against an over-estimation and an improper application of the mathematical treatment of such questions.

There is an evolution of 3.1 calories in this case. If at last cupric oxide is again re-converted into cupric chloride by hydrochloric acid, there is again a liberation of heat:—



The algebraic sum of the calories concerned in the reactions No. 1 to 3 is  $3.2 + 57.3 - 32 = 28.5$  cal., that is a positive magnitude. Hence, if once the reaction has set in, it can go on without any addition of heat or other form of energy as long as HCl and O are supplied.

The dissociation of cupric dioxide (reaction No. 1) will cease as soon as the presence of the chlorine gas has reached a certain limit, increasing with the temperature, as is the case in all reversible reactions. Hence the decomposition of HCl will, up to a certain point, be all the more perfect the higher the temperature. But if once the temperature is reached at which  $\text{CuCl}_2$  can no longer exist, the whole cycle of reaction will be discontinued: then the "catalytic action" of the copper salt on the mixture of HCl and O will cease. Care must therefore be taken not to exceed that upper limit of temperature.

The reactions of the Deacon process, like all reactions among gaseous bodies, are more perfectly carried out, firstly, the more uniform we keep the composition of the gaseous mixture; secondly, the less inert gas is mixed with that which enters into the reaction. Even a large excess of one of the gases really concerned in the reaction acts in a similar way, although usually a *certain* excess of a gas which costs little or nothing (in this instance, of atmospheric oxygen) may be useful.

The decomposition of the hydrogen chloride can be carried all the further the more a useless excess of air is avoided, and the more uniform is the mixture of HCl and air. This is an important factor in Hasenclever's process of expelling HCl from impure hydrochloric acid by sulphuric acid and air (*vide infra*).

The importance of the Deacon process rests on the following points:—In the old manganese-ore process theoretically 50 per cent., practically hardly more than 30 or 33 per cent., of the chlorine of the hydrochloric acid is set free. In the Weldon process the proportion of chlorine utilized is even less in theory,



viz. 40 per cent., but in practice it is about the same as with manganese ore. But in the Deacon process theoretically *all* the chlorine of HCl is obtained in the free state; in practice it is certainly far removed from that. Until the last few years, as long as the roaster-gas could not be utilized, at most 40 per cent. of the HCl was obtained as free chlorine, that is in itself more than in the other processes; and the remaining 60 per cent. were recovered as hydrochloric acid, the greater part of which is strong enough to be utilized for making chlorine by the Weldon process, so that altogether, with good work, not much less than twice as much chlorine is obtained as with the Weldon process alone. At all events this can be achieved by the employment of those processes which admit of utilizing the roaster-acid for the Deacon process. It will hardly be contradicted that that process, since the great mistakes made in bringing it out at first have been overcome, is by far the most advantageous of those chlorine-making processes which are actually working on the large scale. Most other proposed new processes will hardly be able to compete with it; this is also very doubtful of the nitric-acid processes for making chlorine. But it would be certainly too much to say that the Deacon process is the best imaginable of all possible chlorine processes, and it is very probable that it will in the end have to give way to electrolysis. It is at all events a fact, somewhat difficult to explain, that the Deacon process even in England has made but little headway against the Weldon process.

#### *Practical Working of the Deacon Process.*

The hydrogen chloride required for this process was formerly taken exclusively from the saltcake-pans, directly in the form of gas: the roaster-gas could not be utilized for it, as we shall see, and had to be condensed in the usual manner to (impure) aqueous hydrochloric acid. This direct employment of the pan-gas has the great disadvantage that the gaseous mixture, formed by the entrance of air, varies considerably during the operation, since the current of HCl given off in the pan is at first much stronger than later on (Vol. II. p. 316 *et seq.*). This might be equalized to a great extent if two saltcake-pans were employed for each Deacon apparatus to be charged alternately: the strong gas first given off would be conducted into the Deacon apparatus, the weak gas

coming off later on into a coke-tower. This proposal has been actually made, but apparently never been carried into practice, probably on account of the complication and the difficulty of changing the currents.

The hydrogen chloride from the Hargreaves process (Vol. II. p. 271) is too much diluted by nitrogen to be applicable for the Deacon process; its great uniformity would certainly be an advantage.

It seems as if during the last few years the tendency had been to produce greater uniformity of the current of gas in the ordinary saltcake-pan, by gradually running-in the sulphuric acid, &c., and as if by this means the reaction in the "decomposer" had been very much improved.

The *roaster-gas* was formerly entirely excluded from use in the Deacon process, since otherwise the catalytic substance became inactive in a very short time, and the conversion of HCl into chlorine came to a standstill (see below). It was soon recognized that this was caused by the sulphuric acid contained in that gas, but for a long time nothing else could be done than condensing it in the old way by means of coke-towers into aqueous hydrochloric acid and working this up by the Weldon process. After many other attempts to utilize the roaster-gas in the Weldon process had failed, this last was at length satisfactorily solved by Hasenclever's process (Engl. pat. 3393, 1883), described Vol. II. p. 417. This consists in treating impure hydrochloric acid by hot sulphuric acid and air, thus obtaining a mixture of pure gaseous HCl with the quantity of air required for the process. This mixture behaves in the "decomposer" even much better than that coming directly from the saltcake-pans, as it is not in the same way exposed to considerable variations in its composition, but is always of uniform quality: in fact the decomposition with this gas can be driven up to 85 per cent., and it might be profitable to condense even the pan-gas first to liquid acid, and drive the HCl out of this as well by sulphuric acid in the shape of a uniform mixture with air. The question whether such a process would pay or not depends upon the cost of the fresh concentration of the sulphuric acid. With cheap coal and with top-fired pans (Vol. I. p. 660), the cost of the Hasenclever process is 16s. per ton of bleaching-powder; this is not very cheap, but offers an advantage in comparison with the low value of roaster acid.

Péchiney (Engl. pat. No. 1276, 1892) describes a different apparatus for expelling pure HCl from impure acid by means of sulphuric acid. This has been described (Vol. II. p. 419) from the French specification.

A similar object as Hasenclever's is pursued by Solvay (Vol. II. p. 416), who employs a solution of calcium chloride, and by Lunge and Naef (Vol. II. p. 417), who cause impure hot hydrochloric acid to come into contact with hot air in opposite currents. The latter process, as I have been privately informed, has been actually carried out at a large factory, but the patent having been abandoned no certain data can be obtained thereon. The apparatus then proposed by us (but not actually carried out) is described in Fischer's *Jahresb.* 1890, p. 504.

An apparatus patented by Péchiney (Germ. pat. 69081) is evidently a development of the principle enunciated by myself and Naef. A tower is divided into two unequal compartments by a vertical partition. The narrower compartment contains several dishes vertically placed one above the other, the impure acid running downwards over these, and at the bottom entering into the wider compartment which is connected with the top of a Glover tower filled with pebbles, in which the acid further descends and is met by an ascending current of hot air.

All these processes have the disadvantage of not removing the *sulphurous acid* contained in the roaster-gas, which remains with the HCl and in the decomposer is converted into sulphuric acid, and thus exerts an injurious action. Kolb avoids this by a process (Engl. pat. 6500, 1891; Bull. Soc. Chim. 1892 [3] vii. p. 689) not entirely novel in principle. He causes the roaster-gas to pass through a chamber filled with lumps of salt of the kind employed in the Hargreaves process (Vol. II. p. 249) and kept at the requisite temperature of about 450°. Here the HCl is not changed at all, but both the sulphuric and sulphurous acid are retained, and in their place more HCl is added to the gas, which now goes into the "decomposer" (see below). A little free chlorine is formed at the same time through the action of the porous salt lumps on the mixture of HCl and O, all of this with evolution of heat (Vol. II. p. 245). After a certain time the salt lumps are removed long before they are entirely transformed into Na<sub>2</sub>SO<sub>4</sub> (which would be impracticable), and are passed through an ordinary saltcake-furnace, in order to be converted into good saltcake. The last

trace of  $\text{SO}_2$  is removed from the gas by passing it through brick-bats impregnated with magnesium chloride and cupric chloride; here the  $\text{SO}_2$  is transformed into  $\text{MgSO}_4$ . The chamber intended for retaining the acids of sulphur can be either combined with the "decomposer," or placed directly behind the muffle of the roaster and heated by a separate fire: in this case the heat of the gases, as they come from the roaster, is made use of. But this has the disadvantage that the gas must be heated still further; before entering into the decomposer it must be cooled down again, in order to condense the water, and then it must be once more heated.

It is therefore still an open question whether it is best to place the chamber behind the roaster or in connexion with the decomposer.

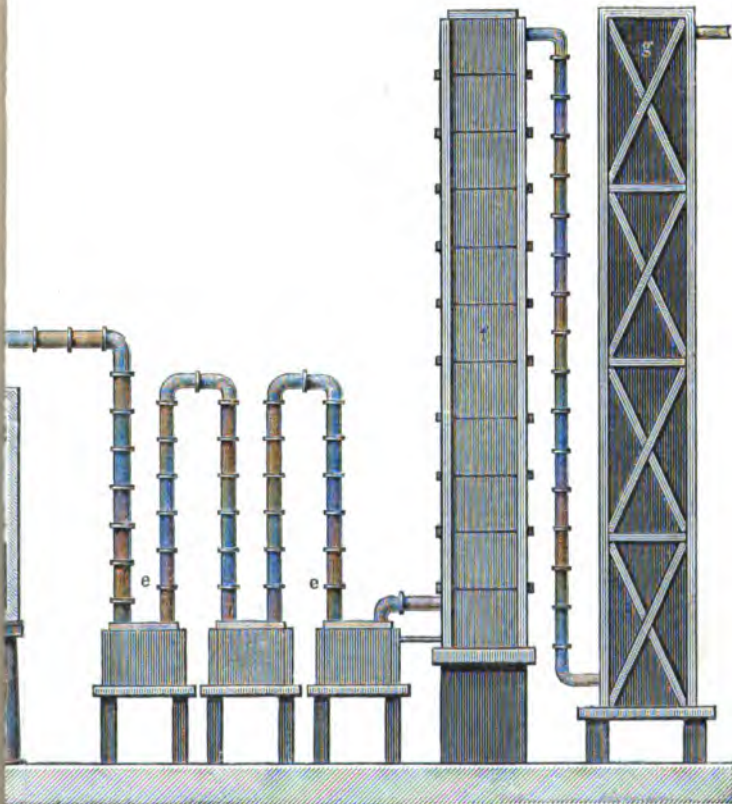
Simpson (Engl. pat. 19776, 1890) believes that the hydrogen chloride obtained by his process (pat. No. 18835, 1890, p. 217), by the action of phosphoric acid on the  $\text{NaCl}$ , is as good as free from nitrogen and therefore specially adapted for the Deacon process.

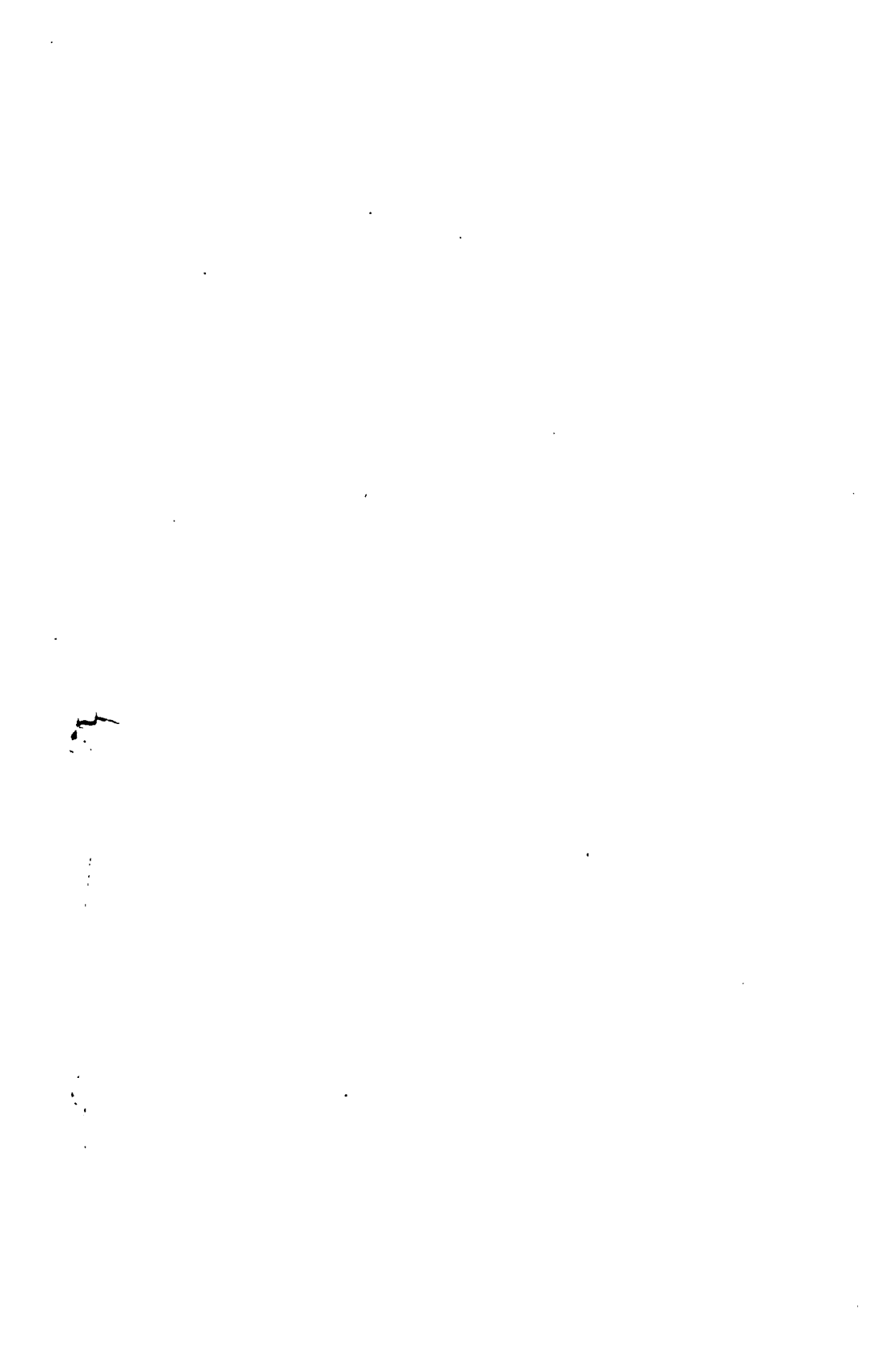
The Deacon process embraces the following essential operations. The acid gas coming from the saltcake-pan, and already there mixed with a sufficient quantity of air, is deprived of great part of its steam by cooling (in which process a somewhat considerable quantity of  $\text{HCl}$  is condensed as well), is then heated in iron pipes to about  $400^\circ\text{C}$ ., and is now passed through an apparatus in which the reaction  $2\text{HCl} + \text{O} = \text{H}_2\text{O} + \text{Cl}_2$  is carried through by contact with lumps of clay impregnated with a solution of cupric chloride. The gaseous mixture issuing from here is freed from the undecomposed  $\text{HCl}$  by washing with water; it is then freed from steam by means of sulphuric acid, and now consists of a mixture of about 5 vol. per cent. chlorine with very much nitrogen and a little oxygen, which is drawn off by a Roots blower and is employed for manufacturing bleaching-powder or chlorates.

#### *The Deacon Apparatus.*

Fig. 131 gives a general outline of the Deacon apparatus, the single parts of which are :—1. The cooling-pipes *a* and the dry coke-tower *b*. 2. The superheater *c*. 3. The decomposer *d*. 4. The condensing-apparatus *e e* with the wet coke-tower *f*. 5. The

[To face p. 384.]





drying-tower *g.* These parts will now be described in detail. A practical "unit" of the Deacon plant consists of the following apparatus:—

1. A *saltcake-pan*, in which 68 to 70 per cent. of the HCl are disengaged from the salt; the remainder of the HCl is expelled in a muffle-furnace, and is condensed in an ordinary coke-tower to liquid acid, which is either treated by the Weldon process for chlorine, or by the Hasenclever process (p. 382) for pure HCl, to be used in the Deacon process as well.

The usual work of a pan is 45 tons of salt decomposed per week; by means of the Deacon plant 18 to 20 tons 36 per cent. of bleach is made from the pan-acid, besides which about 18 tons of hydrochloric acid is recovered (much of it in a dilute state), and all the roaster-acid, unless this is used up as well by means of the Hasenclever process. Theoretically it would be much better to combine two saltcake-pans with each Deacon plant, but this does not seem to be carried out in practice (p. 381).

The *air* required for the reaction is mixed with the hydrogen-chloride gas already in the saltcake-pan, by regulating the speed of the aspirating-apparatus, which acts behind the bleaching-powder chambers, in such manner that the proper quantity of air is drawn in through the pan-door. This is checked from time to time by drawing off a sample of the pan-gas by means of a small aspirator and causing it to pass through standard soda solution, coloured with litmus or some other indicator, and continuing this up to the point where the colour changes. The proportion of the residual air to the HCl found in this way ought to be as nearly as possible equal volumes of air and HCl. In the further progress of the gas the quantity of the air is greatly increased by that which is drawn in through the joints, as we shall see. This to a certain extent promotes the decomposition, but it furnishes dilute chlorine gas.

2. Now follows a *cooling-apparatus*, consisting of a long string of pipes, preferably connected with a small dry coke-tower. Here the gases are as much as possible freed from water by the cooling action of the air. The water, of course, at the same time carries down a certain quantity of acid; according to the strength of the sulphuric acid employed for decomposing the salt and the moisture contained in the salt, the acid condensed here amounts to between 10 and 12 per cent. of the total pan-acid.

The string of pipes is sometimes upwards of 300 feet long. Glass pipes (Vol. II. p. 326) have proved very efficient in this case. The pipes are best followed by a small coke-tower, *not* fed with water, in which the acid mist still floating in the gas is mechanically retained.

The strength of the acid condensed in this cooling-range rarely exceeds  $26^{\circ}$  to  $28^{\circ}$  Tw., and in the case of wet salt it is below this. It is usually worked up in a Weldon plant.

As the drying of the gas is nothing like complete in this way, and it is preferable to introduce the gas into the decomposer as dry as possible, Deacon and Hurter (Engl. pat. 2104, 1888) propose placing a tower fed with strong sulphuric acid behind the cooling-apparatus.

The same inventors (Engl. pat. 15063, 1888) describe another way of preparing dry HCl gas for the Deacon process, viz., to add common salt to sulphuric acid and to blow in air by means of a pipe reaching below the liquid mass and ending with a rose. Thus the air is dried, and the agitation of the acid sulphate by the current of air aids in the decomposition.

There seems to be no doubt, both theoretically and practically, that the action of the "decomposer" is all the more perfect the drier the gases enter into it.

3. The gases now enter into the *heating-apparatus*. This is a furnace 16 feet square, in which 24 vertical pipes, 12 inches wide and 9 feet high, are arranged in two sets of 12 each, so connected that as little resistance as possible is offered to the gas passing through. This arrangement will be better understood from the plan, fig. 132, which will make it clear that this heater is a close copy of the hot-blast stoves for the blast in pig-iron-smelting, according to the "breeches" pattern formerly in use for that purpose. A is the fireplace; B B, flue conveying the heat; B', a chimney within the furnace, conveying the flame one foot above the bends of the heating-pipes D D; C, holes in the bottom for the exit-smoke. Here the gases are heated up to  $400^{\circ}$ ; the waste heat of this furnace is employed for heating the decomposer, which does not possess any fire of its own.

Figs. 133 and 134 show a simpler form of iron hot-blast stove; and it goes without saying that any other shape of this well-known apparatus may be used here.

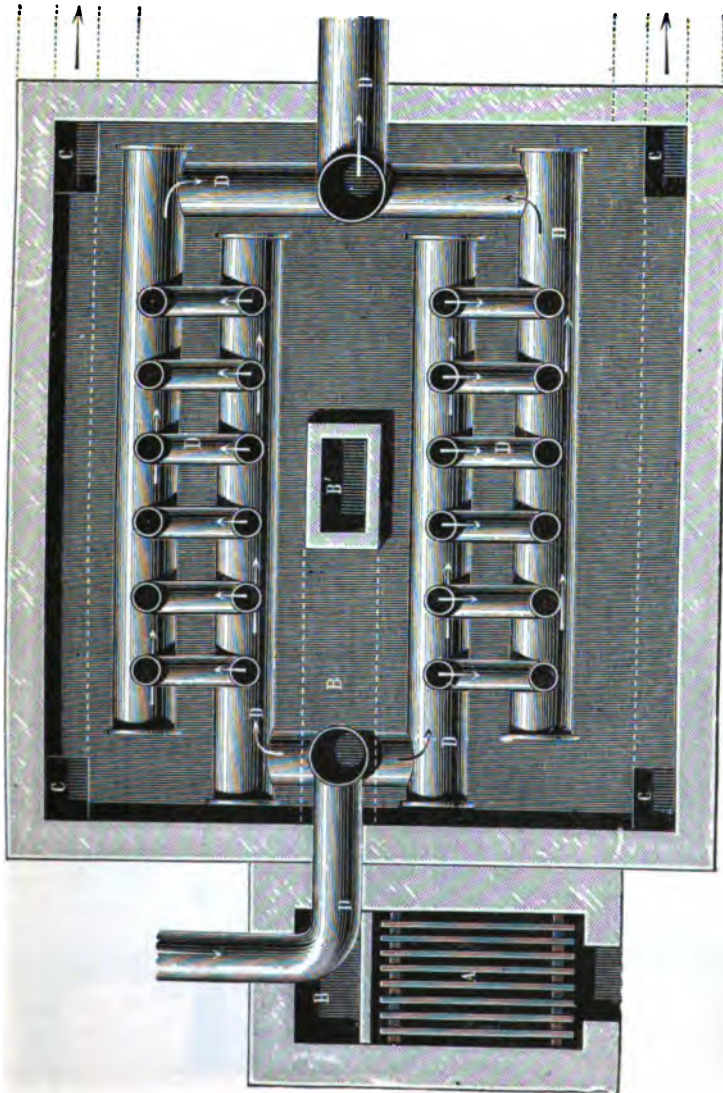
In all cases the fuel gases, after leaving the heating-stove, are



carried round the decomposer, which does not possess a fireplace of its own.

Instead of iron superheaters it is proposed in Péciney's patent, No. 22320, 1891, to employ the well-known Cowper or Whitwell

Fig. 132.



stoves, constructed of brickwork, and now almost universally used for blast-furnaces. In these a higher temperature can be

Fig. 133.

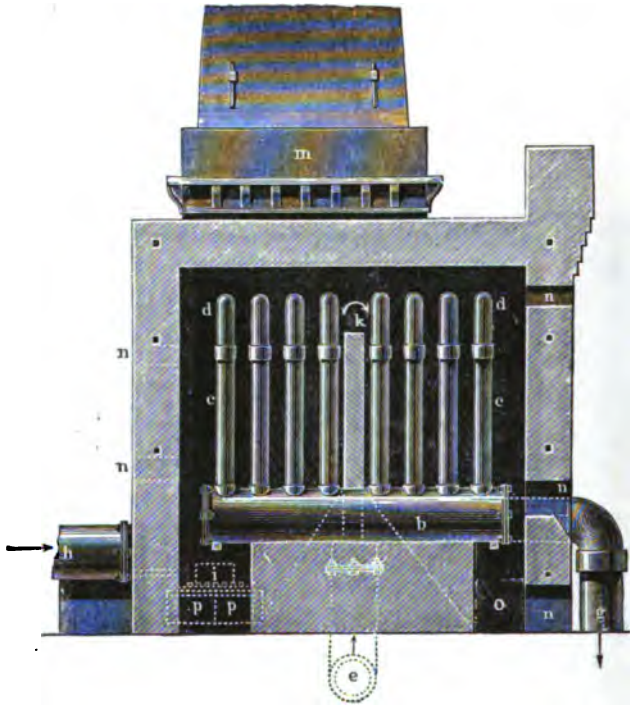
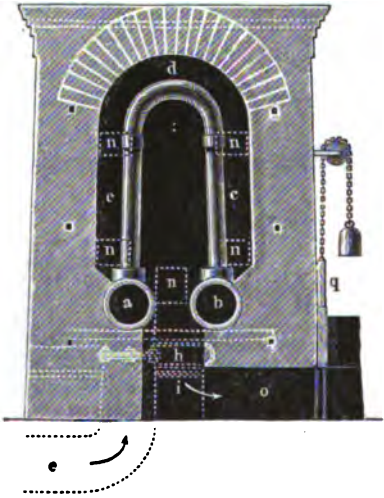
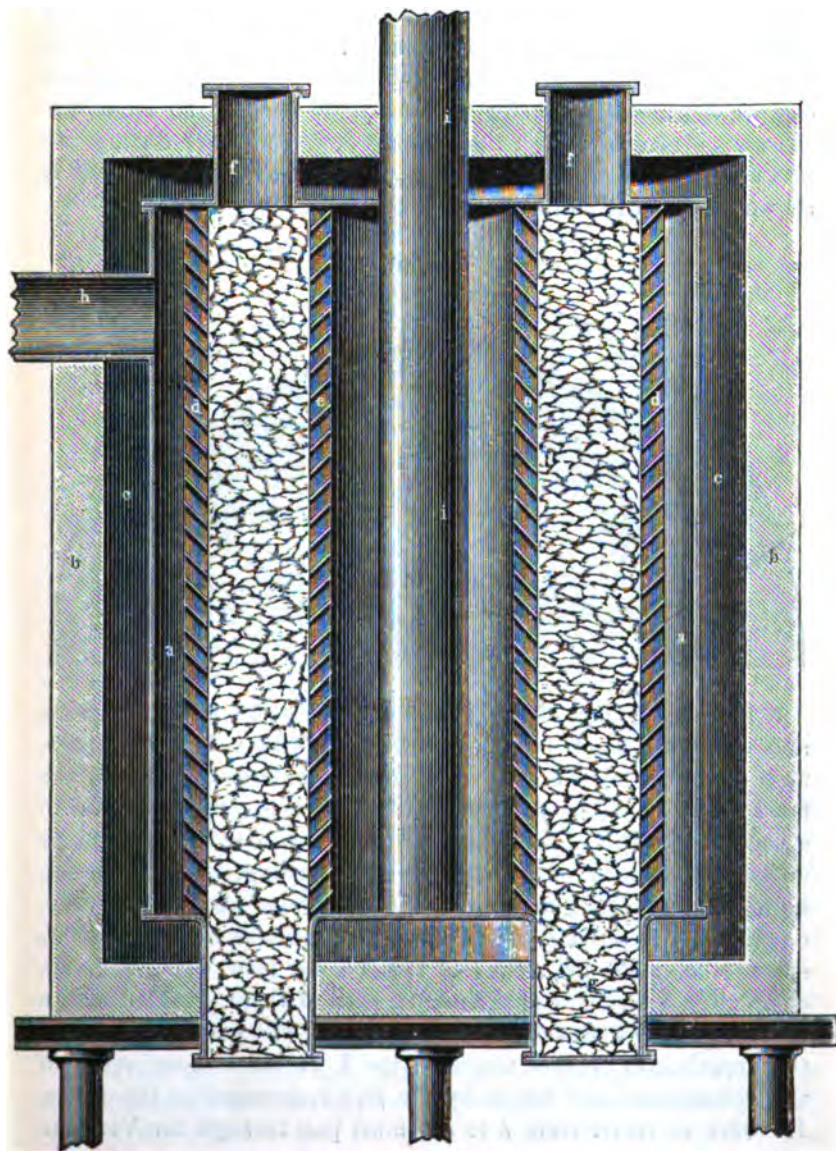


Fig. 134.



attained; there is less wear and tear, and a cheaper catalytic substance can be used, like De Wylde and Reychler's (see below).

Fig. 135.

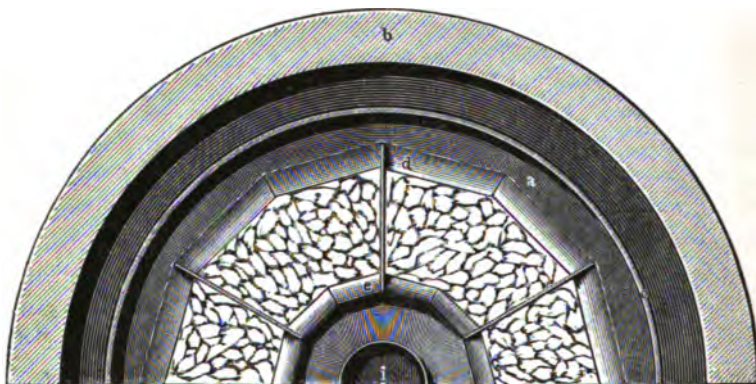




It is usually stated that the heating of the gases is to be carried to a temperature of  $400^{\circ}$ ; but in reality  $450^{\circ}$  to  $470^{\circ}$  C. is nearer the truth.

4. The *Decomposer*.—The original shape of this, the most important part of the Deacon apparatus, as illustrated and described in our first edition, Vol. III. p. 253 *et seq.*, was altogether a technical failure, and this mistake in chemical engineering has undoubtedly to bear great part of the blame for the want of success which that process suffered under during the first stage of its progress. The modern shape of a decomposer is shown in figs. 135 and 136.

Fig. 136.



A large upright cast-iron cylinder *a*, from 12 to 15 feet wide and about the same height, is surrounded by a brick jacket *b*, flues *c c* being left between this and the cylinder, in which the hot fire-gases coming from the heating-stove (p. 386) are made to circulate. Within the cylinder there is a double octagon or dodecagon, formed of iron plates *d, e*, arranged like Venetian blinds and enclosing an approximately annular space, 3 feet wide, destined for receiving the catalytic substance (see below). This space is divided, by means of radial solid iron walls, into six completely separated compartments, each of them provided with a charging-hole *f* and a discharging-hole *g*. The gas, heated up in the superheater, enters through pipe *h* at the circumference of the decomposer, and leaves by the pipe *i*, arranged in the centre. In order to travel from *h* to *i* it must pass through the Venetian

blinds *d* and *e* and through the contact substance contained between these, and here it is decomposed according to the reaction  $2\text{HCl} + \text{O} = \text{H}_2\text{O} + \text{Cl}_2$ , although not completely. From *i* escapes a mixture of  $\text{Cl}$ ,  $\text{HCl}$ , steam,  $\text{N}$ , and the excess of  $\text{O}$ , and this passes on to the cooling-apparatus (see below).

Each of the six compartments contains six tons, and the whole decomposer 36 tons of broken bricks. Every fortnight one of the compartments is emptied, so that the whole of the contents are exchanged once every twelve weeks.

Brock, Driffield, and Wright (Engl. pat. 11966, 11967, and 11968, 1894) describe several modifications of the ordinary shape of decomposers.

The *temperature* within the decomposer must be measured by a pyrometer. For such temperatures as are here referred to ( $450^\circ \text{C.}$ ), several very suitable pyrometers have recently been constructed; even mercury thermometers filled with nitrogen can be used here, or those which are filled with an alloy of potassium and sodium. Hurter (Journ. Soc. Chem. Ind. 1886, p. 634) recommends an air-pyrometer constructed by Heisch and Folkard; he recognizes, however, its liability to breaking, and points out that exact indications can be obtained only by the calorimetric method ('Alkali-makers' Hand-book,' 2nd ed. p. 90), which is, however, too troublesome for daily use\*.

The pyrometers formerly used at the works (including Deacon's metal pyrometer) were very unreliable and not constant in their indications. This partially explains the discrepancies in the statements formerly made on the temperature within the decomposer, which varies between  $370^\circ$  and  $450^\circ$ . The second figure seems to be nearer the truth.

The regulation of the temperature of the decomposer is effected almost entirely (or quite) by the fire of the superheater. In the large mass of clay contained in the decomposer variations of temperature can only occur gradually, so that the apparatus is to a great extent self-regulating. This can be promoted by suitable dampers.

Rommert (Germ. pat. 59556) proposes to effect a better utilization of the heat of reaction in the decomposer by reversing

\* We can now obtain thoroughly reliable pyrometers, among which that of Le Châtelier, as supplied by Keiser and Schmidt of Berlin, probably holds the first rank.

the direction of the gaseous current as soon as the contact mass has reached the highest temperature at the end of the apparatus. The reaction thus goes on more regularly, and there is a saving of fuel. For this purpose the main pipe through which the heated gas enters must be arranged in such way that the gases can pass in either at the top or at the bottom, and the exits must be arranged in a similar manner.

The *catalytic* or *contact-substance* formerly consisted of balls of porous clay, "marbles," which were impregnated with a copper salt. Considering the large quantity of this material and the necessity of frequently renewing it, its cost was somewhat heavy. A patent by Deacon (No. 1632, 1875) proposed replacing it by lumps of burnt pyrites, but this does not seem to have answered. At all events the factories have long since gone over to broken bricks of irregular shape. Where waste brick-bats are not to be obtained in sufficient quantity, clay is burnt in lumps; it is then coarsely broken up by a Carr's disintegrator and the dust sifted out; these bits of clay are then impregnated with the copper salt ("dipped").

In the beginning the dipping was performed by sulphate of copper, which was expected to be converted into chloride by the HCl and the chlorine; but this did not prove suitable. In 1873 (No. 505) Deacon patented the application of a magnesium copper sulphate; in 1875 (No. 1909) an addition of magnesium sulphate; in the same year (No. 906) the application of cupric chloride, or of a mixture of NaCl and CuSO<sub>4</sub>, in which case the decomposition is stated to take place more regularly, at a lower temperature and with less volatilization of copper than with CuSO<sub>4</sub>. In fact at the present day cupric chloride is everywhere employed as contact-substance, and is obtained by dissolving copper ashes in hydrochloric acid; this admits of keeping the temperature in the decomposer 80° lower than with cupric sulphate (comp., however, Gaskell and Carey's patent of 1893, *infra*).

In order to prevent the loss of "catalytic force" by the volatilization of the copper salt or its soaking into the interior of the marbles, Deacon further proposed to cool down the decomposer now and then to 150° C., and to inject steam, which dissolves the copper salt and divides it equally over the marbles. This proposal has not answered its purpose, no more than that patented by him in 1876 (No. 1927), to absorb the HCl escaping undecomposed

from the decomposer by ferric oxide, dipped in a solution of cupric sulphate and piled up in upright cylinders; after the absorption has taken place, air heated to the requisite temperature, or a mixture of air and HCl, is passed over the mass, which then acts as a contact-substance.

Blattner and Kestner (Chem. Zeit. 1893, p. 466) found that a mixture of from 4–7 vols. air to 1 vol. HCl, heated to 520° or 530° C. and passed over cinders from cupreous pyrites, containing from 1 to 2·7 per cent. Cu, caused a decomposition of from 50 to 60 per cent. of the HCl. Only so much HCl was retained by the contact substance as corresponds to the copper, which was therefore mostly rendered soluble in water. On the small scale 200 to 250 grams chlorine were obtained from 1 kil. cinders in 24 hours (in the Deacon process on the large scale only 70 grams Cl are obtained per 1 kil. mass). This process cannot be carried out with an ordinary Deacon plant, as the cinders are too irregular in shape and too heavy; according to the inventors' own view it is mostly adapted for such cases where the copper extraction from cinders is the principal aim.

The quantity of the copper taken up by the burnt clay varies between 0·7 and 1·2 per cent., calculated as metallic Cu; mostly it is in the fresh state = 0·75 per cent.; the spent mass contains only 0·2 to 0·3 per cent. Cu.

Whatever description of contact-substance is employed, it is certain that none of them acts continuously or even for a very long period; the misadventures which during the first years occurred with the Deacon process are mostly ascribable to an insufficient recognition of this point. The marbles impregnated with cupric sulphate refused everywhere to act continuously as a contact-substance. After a comparatively short time the decomposition of hydrochloric acid, *i. e.* the production of chlorine, begins to decrease; and this goes on till the action ceases altogether. This sometimes happened almost directly; usually it took some time, though rarely more than four months from the time of commencement. This cessation of the action of the marbles was attributed to various causes, such as the volatilization of cupric chloride, the incrustation of the pores by ferric chloride, sulphate, soot, flue-dust, &c. Be this as it may, nothing remained to be done, except stopping the work, discharging the decomposing-pans, and redipping the marbles in cupric

sulphate. This cost several hundreds of pounds—that is hardly ever less than £1 per ton of bleach made. Moreover these stoppages, amounting usually to 8–14 weeks per annum, were almost unbearable, owing to the interruption of all other operations connected with this. The hydrochloric acid mostly had to be run away; interest and royalty were running on all the time; and much inconvenience was caused by non-fulfilment of contracts. Worst of all, the decomposer, after redipping, never worked so well as at first, sometimes not at all, and so the work could not be carried on.

The reason why the contact-substance in the Deacon decomposer gradually ceases to act has been principally elucidated by the researches of Hasenclever. He found (*Deutsch. chem. Ges. Ber.* ix. p. 1070) that this takes place without any considerable loss of copper in the marbles. At the Rhenania works the decomposition of the HCl, which for some weeks had amounted to 60 per cent., suddenly fell within three days to 2 per cent. The marbles now contained upon 1·2 per cent. copper 8 per cent.  $\text{SO}_3$ , instead of 1·5 as required by the formula  $\text{CuSO}_4$ . It would thus seem that the marbles retain the sulphuric acid contained in the gases, and when they are saturated with it the decomposition ceases—possibly because the marbles are covered with a layer of sulphate, or because the  $\text{SO}_3$  in contact with red-hot sulphates splits up into  $\text{SO}_2$  and O, which with Cl and steam produce again  $\text{H}_2\text{O}$  and HCl. In all probability the varying duration of the activity of the decomposers (from  $1\frac{1}{2}$  to 10 months) in the different works depends on the percentage of sulphuric acid in the decomposing gases. The pan-gas contains only 1·5, the roaster-gas 7·5,  $\text{SO}_3$  per 100 HCl. In fact a works where only the pan-gas was employed, and, moreover, partly purified from sulphuric acid in a stone cistern, went on for 10 months; another, employing ordinary pan-gas, 5 or 6 months; the Rhenania works, where also the roaster-gas was employed, only  $1\frac{1}{2}$  month. Starting from this reasoning, Hasenclever (No. 4291, 1874) took out provisional protection for purifying the decomposing-gases from sulphuric acid by lime, alumina, common salt, &c., before admitting them into the decomposer—and again (No. 2109, 1875) for washing out the sulphuric acid or removing it by partially condensing the gas. The latter, however, had been already patented by Deacon himself (No. 2003, 1875).



Jurisch also furnished a contribution to this question (Dingler's Journal, ccxxi. p. 356). He states that the principal reason why the majority of English works had given up the Deacon process was the trouble caused by the redipping of the marbles, which become the less active the oftener they are treated—also in the quick wear and tear of the whole apparatus, which renders the process more expensive than Weldon's. Whether working quickly or slowly, the general [?; comp. Hasenclever] production for 120 tons of marbles with about 1 per cent. copper is 600 tons of bleaching-powder. He finds inactive marbles to contain 0.92 per cent.  $\text{CuSO}_4$ , 5.86  $\text{Fe}_2\text{Cl}_6$ , 75.30  $\text{Fe}_2(\text{SO}_4)_3$ , &c. The dust accumulated between them contained 71.70 per cent.  $\text{Fe}_2(\text{SO}_4)_3$ , 13.64  $\text{Fe}_2\text{O}_3$ , &c. The hydrochloric acid condensed in the first cooling-vessels contained per litre 329.3 grams  $\text{HCl}$  and 20.78 foreign constituents, among them 9.376  $\text{H}_2\text{SO}_4$ , 0.368  $\text{CuCl}_2$ , &c. Only from 15 to 25 per cent. of the copper is lost by volatilization. The cause of the loss of activity must hence be sought elsewhere; and this is done by Jurisch in the incrustation of the marbles by impurities, partly from the sulphuric acid used in decomposing, partly from the marbles themselves. Most dangerous are the sulphates of iron and aluminium; next to these, ferric chloride and arseniates. The sulphuric acid ought to be purified from arsenic, and the formation of iron and aluminium sulphates prevented, as these constitute 80 per cent. of the incrustations. The sulphuric acid found comes partly from that usually added in dipping the marbles, partly from that evaporated in the decomposing-pans. Roaster-gas ought never to be employed, because it contains too much sulphuric acid and other impurities; of the pan-gas only the first portion, which upon 100  $\text{HCl}$  contains from 0.251 to 1.079  $\text{SO}_3$ , but later on, when the batch in the pan stiffens, as much as 8.723  $\text{SO}_3$ . It is consequently best to work with two pans, each alternately sending its gas into the apparatus so long as it is still fresh and the batch thiu (comp. pp. 381 and 385). In order to increase the activity of the marbles on redipping, they are to be broken up and also exposed to the atmosphere in heaps for several months. The sulphuric acid is most injurious in the state of vapour, less so when it is retained by bases ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ) in the marbles; but when the bases are saturated the decomposition ceases. In any case most of the sulphuric acid passes through undecomposed, as is proved by its presence in the hydrochloric acid condensed behind the decom-

poser. Hence it is a vital question for the Deacon process, either to remove the sulphuric acid out of the gases, or to employ a large quantity of base as carrier of the active substance, *e. g.* ferric oxide as burnt pyrites [already patented by Deacon, in 1875, p. 392]. Jurisch mentions that English manufacturers had endeavoured to remove the sulphuric acid by partial condensation of the gas, but unsuccessfully, as too much HCl was condensed as well. Direct laboratory experiments (cited in detail) proved that the decomposition suddenly fell, on the introduction of sulphuric-acid vapour, from 39.72 to 13.72 per cent. Here the incrusting action of the sulphates could not yet have come into play; and hence the action of retarding or entirely preventing the formation of Cl from HCl must belong to the sulphuric acid in the state of vapour. This conclusion was afterwards entirely withdrawn by Jurisch (ib. ccxxii. p. 366), Hurter having proved to him the incorrectness of his experiments. Hurter states that sulphuric acid acts far less injuriously than is believed, but, similarly to arsenic and antimony, it acts by converting the copper into unchangeable compounds; the decomposition goes on *pari passu* with the volatilization of cupric chloride.

Hasenclever, in opposition to Jurisch, states (ib. p. 256) that even before the latter he had recognized the injurious action of sulphuric acid, that he had everywhere found the hydrochloric acid escaping undecomposed out of the decomposer free from sulphuric acid, and that the attempts of some English manufacturers (mentioned by Jurisch) to remove the sulphuric acid by partial condensation were only accidental operations, in which the damage caused by that acid was not at all recognized.

To this Jurisch replied (ib. p. 567), admitting Hasenclever's claim to priority as to the injurious action of sulphuric acid, but contesting the fact that the HCl escaping undecomposed is free from  $\text{SO}_4\text{H}_2$ , except for a very short time at the commencement of a period; he also cites several instances of English manufacturers introducing a partial condensation of their hydrochloric acid and with it a purification from sulphuric acid. Hensgen's research (cited on p. 40, Vol. II.) should also be compared here.

Lequin (French Exhib. Report, 1891, p. 83) mentions that at Deacon's works they had for some time past interposed a "purifier" in front of the decomposer, in which the gases pass through a horizontal layer of bits of clay soaked with copper salt: here they

give up their sulphuric acid, and the decomposer now continues operating much longer without change, while the mass in the "purifier," where about one-fifth of the chlorine is made, must of course be renewed much more frequently.

The same object is pursued by the process of Kolb (p. 383), in which the  $\text{SO}_2$  and  $\text{SO}_3$  are retained by sodium chloride.

The injurious action of the sulphuric or arsenious acid on  $\text{HCl}$  is to be checked, according to Gaskell and Carey (pat. No. 25024, 1893), by adding to the contact mass such substances as have more affinity for those impurities than copper, viz. calcium or magnesium chloride (comp. already Deacon's patents of 1873 & 1875, p. 392). In this case the clay, before being burnt, is mixed with up to 7 per cent. of a basic substance, as quicklime, calcium carbonate, magnesia, or limed mud from the caustic soda or the Chance process.

The most thorough remedy against the damage done by the sulphuric acid is, of course, its removal from the  $\text{HCl}$  by the means quoted, pp. 382 and 383. But even then the arsenious acid remains to be dealt with. Apart from this, there is in every case a gradual volatilization of copper, and therefore nothing remains but to abandon an indefinitely prolonged use of the contact-substance, and to *renew the clay lumps, impregnated with copper salt, at regular intervals*. Deacon (No. 332, 1875) patented for this purpose a continuously acting discharging-apparatus, which has found no practical application. The solution of this problem ultimately found is shown by the above described shape of the decomposer (p. 390), whose polygonal space is divided by partitions into six compartments, each of which is provided with necks at top and bottom. Without interrupting the work, any one of these compartments can be emptied from below and recharged with fresh material from the top. This is done once a fortnight with one of the six compartments, so that the whole mass is renewed every twelve weeks (p. 391). The compartments are always entirely emptied; a partial emptying and refilling has not been found to answer.

According to prolonged experience the regular renewal of the contact-substance involves, per ton of 35 per cent. bleaching-powder, the consumption of about 4 cwt. of burnt clay, and of 3 to 4 lbs. copper according to its percentage in the clay.

Many attempts have been made, but unsuccessfully, to turn the

waste lumps of clay to use again by redipping, or else to extract the 0.2 or 0.3 per cent. of copper contained therein; they are simply thrown away. A recent patent, however, by Wilde and Williams (No. 21412, 1893), states that they can be used over again by washing with hydrochloric acid of 5 per cent. and drying; the copper can be precipitated from the solution by metallic iron. [It seems very unlikely that this process should not have been tried before.]

Hargreaves, Robinson, and Hargreaves (Engl. pat. 5673, 1886) try to promote the decomposition by mixing the HCl gas while hot with a little vapour of cupric chloride. Any  $\text{CuCl}_2$  carried away as vapour from the decomposer is subsequently condensed in the coke tower, and is always recovered when employing the condensed acid from this tower for the manufacture of chlorine by the method to be described below [?]. The strong chlorine gas thus obtained is introduced into the ordinary Deacon chambers, to act together with the weak chlorine. Such strong chlorine is to be obtained by passing a little of the weak chlorine into milk of lime and decomposing the solution of calcium hypochlorate thus formed by the weak acid coming from the wash-tower. [This process seems to be rather troublesome and expensive.]

*Testing the gases from the decomposer.*—These gases consist of undecomposed HCl, free chlorine, steam, oxygen, and nitrogen. They are usually only tested for the first two constituents, which at Deacon's works is done as follows:—Aspirate 5 litres of gas, issuing from the decomposer, placing the apparatus as closely to the outlet as possible, and absorb the HCl and Cl in a solution of caustic soda of 15° Tw., of which about 250 cub. cent. are distributed into two or three absorbing-bottles. The time of absorption ought to agree with the time occupied by the charge in the saltcake-pan. Unite the contents of the several bottles and dilute to 500 cub. cent.

(1) Take 100 cub. cent. of this solution, and add it gradually to 25 cub. cent. of an iron solution (prepared and standardized as directed on page 277) in a flask provided with a Bunsen valve, and heat to boiling. Allow to cool, dilute with 200 cub. cent. of water, and titrate with semi-normal permanganate solution. Say it required  $y$  cub. cent. Suppose that when standardizing the iron solution 25 cub. cent. of iron solution required  $x$  cub. cent.

(2) Take 10 cub. cent. of the solution to be tested, add thereto some solution of sulphurous acid, acidify with dilute sulphuric acid. If it does not smell of sulphurous acid, add a little more. Heat to boiling. When cool, add, if necessary, a few drops of permanganate to oxidize any sulphurous acid in excess. Neutralize with pure carbonate of soda, dilute with water, and, after adding a few drops potassium chromate, titrate with decinormal silver solution. Suppose it consumes  $x$  cub. cent. of silver solution. Then

$$\frac{50x-y}{z}$$

is the percentage of hydrochloric acid decomposed, and

$$\frac{42.5 + \frac{x-y}{8}}{z}$$

equals the amount of air present for every volume of hydrochloric acid. If any other volume  $l$  of gas instead of 5 litres be employed, the constant 42.5 changes into

$$\frac{l \times 1.55}{50 \times 0.00365},$$

assuming that the other directions are strictly followed, and that 1 litre of hydrochloric acid weighs 1.55 grm. at 50°C. and 760 millim. pressure.

Younger (Journ. Soc. Chem. Ind. 1889, p. 88, and 1890, p. 159) objects to this method that the absorption of the gases on principle involves an error. He therefore proposes to aspirate the gaseous mixture through an aqueous solution of arsenious acid, to which a few drops of indigo solution have been added as an indicator. The aspiration of gas is continued till the indicator is just discoloured, and the water run out of the aspirator is measured (just as in the testing of pyrites burner-gas for  $\text{SO}_2$ , Vol. I. p. 324). Thus the quantity of chlorine per unit volume of the gas is easily calculated; that of  $\text{HCl}$  is found by titrating the same liquid with silver nitrate and deducting from the total  $\text{HCl}$  that corresponding to free chlorine. [Younger does not mention how the titration is to be performed when following his process; we shall therefore describe this operation. It is best to neutralize with pure sodium carbonate, a small excess of which does no harm, and decinormal silver solution is added, with stirring, until the white colour of  $\text{AgCl}$  shows a pink shade. In this case, as I pointed out many years

ago, the arseniate serves as indicator, similar to Mohr's potassium chromate, and it is even more sensitive than this.]

If the *steam* contained in Deacon-gas has to be estimated as well, a U-tube, filled with pumice soaked with strong sulphuric acid, or else a bulb-apparatus charged with such acid, is interposed between the gas-pipe and the apparatus destined for absorbing Cl and HCl; the increase of weight of the apparatus containing the sulphuric acid indicates the quantity of  $H_2O$ . This estimation is more exact if before the weighing dry air is aspirated for some time through the drying-apparatus, in order to expel any chlorine and HCl from the sulphuric acid; it is best in this case to place a second, weighed, sulphuric-acid tube behind the first.

*Carbon dioxide* is estimated by absorbing the gases in caustic soda solution, destroying the hypochlorite by boiling with ammonia, and estimating  $CO_2$  by the well-known methods.

*Action of the decomposer.*—According to Hurter (Dingl. Journ. ccxxiii. p. 71) the decomposition can be made almost complete in the laboratory; but on the large scale it but rarely amounts to 60 per cent. of the HCl, especially when the apparatus have become leaky. Except in quite new and perfectly tight apparatus, a total decomposition of 45 per cent. must be acquiesced in, if the mixture was composed of equal volumes of air and HCl gas with a little steam. The quantity of chlorine produced, if the other conditions remain the same, is nearly proportional to the geometrical means of the quantity of HCl and air present. If the HCl contained in a unit volume of the mixture be called  $x$ , and the air  $y$ , the quantity of chlorine Cl, if  $c$  denotes a constant, is  $Cl = c\sqrt{xy}$ . Since with incomplete decomposition or with a very large excess of air the tension of the chlorine gas produced becomes about  $\frac{Cl}{y}$ ,

we have  $\frac{Cl}{y} = c\sqrt{\frac{x}{y}}$ . Hence the tension of the chlorine gas is subject to much smaller variations than that of the hydrochloric-acid gas employed for its generation. Usually there is  $1\frac{1}{2}$  vol. air present to 1 vol. HCl: this in the case of complete decomposition yields  $\frac{1}{2}$  vol. Cl, or with 50 per cent. decomposition (*i. e.* in a *very* good apparatus)  $\frac{1}{4}$  vol. Cl, which, mixed with the remaining N and O, yields dilute chlorine with about  $\frac{2}{3}$  vol. = 15 per cent. chlorine. [The last mentioned strength is never reached, as we shall see.]

Recently a better decomposition has been attained. With a totally

new charge of copper-soaked bits of clay it is possible to get up to a decomposition of 88 per cent. ; also with the pure HCl obtained in the Hasenclever process, p. 382. With an older mass only 25 per cent. is reached, and with regular renewals of the mass the average decomposition is 67 per cent., that is, two-thirds of the HCl is transformed into free chlorine.

Kolb (Bull. Soc. Chim. 1892, [3] vii. p. 789) represents the conditions of the process as follows:—Pan-gas on an average contains 50 vols. per cent. HCl, 25 H<sub>2</sub>O, 25 air (comp., however, Vol. II. p. 315). On cooling (p. 385) the water is condensed, and takes along 10 per cent. of the HCl, so that 90 per cent. of the HCl is left. This, on entering the decomposer, has been diluted by more air being drawn in, so that we have there 1 vol. HCl to 3 vols. air. The gas leaving the decomposer is, on an average, composed of 8 volume per cent. chlorine, 9 per cent. HCl, 8 per cent. H<sub>2</sub>O, 75 per cent. air. Since each vol. Cl<sub>2</sub> corresponds to *two* vols. HCl, the above means that two-thirds of the HCl has been transformed into Cl and H<sub>2</sub>O; this can be attained by a regular change of the contact-substance, involving a consumption of 1 kil. CuCl<sub>2</sub> to 800 or 1000 kil. bleaching-powder.

By the condensation (see below) the HCl vapour and steam, together 17 vols., are removed; the remaining 83 vols. contain 8 vols. chlorine, or about 10 vol. per cent. But since later on more air is drawn in, practically the gas only contains 5 to 7 vols. chlorine to 93 to 95 vols. air.

Altogether in the Deacon process, of each 100 kils. of HCl escaping from the saltcake-pan, 60 are converted into 60 free chlorine and 40 recovered as hydrochloric acid; or, as the pan-acid amounts to  $\frac{3}{4}$  of the total acid, 40 kils. of the latter are obtained as chlorine, 27 as recondensed acid (partly weak), and 33 as roaster-acid.

With roaster-gas by itself the case is much less favourable. Kolb assumes it to contain on an average 20 vols. per cent. HCl, 40 H<sub>2</sub>O, and 40 air. From this on cooling, 40 per cent. of the HCl is condensed as strong acid, with 2 to 5 per cent. sulphuric acid. The remaining gas is diluted with more air and arrives in the condenser as a mixture of 1 vol. HCl with 9 air, that is, three times more dilute than pan-gas. In the decomposer it yields a mixture of 3 vols. Cl, 3 HCl, 3 H<sub>2</sub>O, 91 air, from which by cooling acid of 23° to 28° Tw. is condensed. If the total HCl were

to be treated in the Deacon apparatus, according to the above calculation 52 per cent. would be obtained as Cl and 48 per cent., less losses, as recovered HCl. This is practically impossible; less on account of the dilution of the roaster-gas (good bleach can be made with 2 or 3 per cent. gas) than on account of the sulphuric acid contained in the latter, which quickly renders the contact-mass inactive by stopping up the pores with sulphates of lime, iron, and alumina. Hence the roaster-gas must not be employed unless it is purified by Kolb's process (p. 383), or the acid made from it is treated by one of the processes mentioned, pp. 382, 383.

5. *Removal of the unchanged Hydrogen Chloride from the Gaseous Mixture.*—Since the gases on leaving the decomposer again contain a considerable quantity of aqueous vapour, much liquid hydrochloric acid must be condensed by merely cooling them. But this does not suffice for removing the HCl, which must be done by washing with water. (Deacon's proposal, p. 392, to absorb the HCl by ferric oxide impregnated with cupric sulphate, and to liberate chlorine from it by heated air, has not answered in practice.)

Consequently the decomposer has to be followed by a complete condensing apparatus for hydrochloric acid; and as such nearly all the apparatus described in the 7th chapter of Vol. II. are employed at different works. In order to produce good bleaching-powder, the arrangement must at all events act perfectly in removing the HCl from the gases, and this is actually achieved in every working Deacon plant. But the results differ very much in another respect. Some manufacturers formerly obtained nothing but weak acid in this way, say 15° to 18° Tw.; others a little strong with much weak acid; but others again made nearly the whole of the acid strong enough to be employed in the Weldon process, or even for sale.

It should not be lost sight of that a washing-arrangement which is perfectly sufficient in regular work (that is, with an adequate decomposition of HCl) will not suffice for removing all the HCl if, in consequence of bad draught or of any mishap to the decomposer, there is bad decomposition, and therefore an excess of unchanged HCl.

The strength of the acid obtained depends entirely upon the apparatus employed for condensation. If this is rationally constructed, with good preliminary cooling by strings of earthenware



or glass pipes, followed by a series of cisterns or earthenware receivers, and ultimately a coke-tower, or better still a plate-tower (Vol. II. pp. 382, 916), with a complete arrangement of opposite currents for the water and the gas, most, if not all, the HCl will be recovered as strong acid.

The German works, especially the Rhenania at Aachen, have been much more successful in bringing up the acid, condensed from the undecomposed HCl, to full strength than, at least formerly, the English works, which generally obtained too much dilute acid. This probably led to the patent of Deacon and Hurter, No. 2311, 1888, according to which the gases, instead of washing them with water, are made to ascend in a tower filled with pebbles, through which Weldon mud descends in such quantity that at the bottom a little undecomposed black mud remains, which is then worked up in an ordinary Weldon still.—This process seems to offer evident advantages at works which possess both a Weldon and a Deacon plant (for others it is, of course, out of the question), as it would do away with the cumbrous condensing-apparatus; the HCl would be completely utilized, and the weak Deacon gas would be strengthened by Weldon chlorine. But it is doubtful whether such a pebble-tower can be fed with Weldon mud without being obstructed. There is, at all events, no technical impossibility in realizing the above principle, even if a pebble-tower should not be found to answer the purpose. I am not aware whether this process is really at work, but I do not believe it is.

6. *Drying the Chlorine Gas.*—The gases freed from hydrochloric acid, if intended for the manufacture of bleaching-powder, must now be *dried*; but if they are passed into milk of lime, to make bleach-liquor or chlorate of potash, no drying is necessary. Formerly for this purpose a tower filled with calcium chloride was employed. This caused great trouble, and the drying was very incomplete. It is now done by a leaden tower packed with coke, in which strong sulphuric acid trickles down. Every trace of water in the dilute chlorine of Deacon's process is injurious and should be removed (Hurter, *Dingl. Journ.* cccxiii. p. 429), chiefly because it forms a layer impermeable to the gases in the lime-chambers; it also assists in the formation of calcium chlorate.

Formerly the sulphuric acid was employed at a strength of

142° Tw., and it was allowed to go down to 120° before being removed for concentration; but it has been found better to use acid of 150° Tw.

The dilute sulphuric acid formed in the drying-tower must, of course, be always re-concentrated. This is generally effected by means of a Glover tower, which is easily done, since Deacon chlorine is always made at works where sulphuric acid is also manufactured.

The consumption of strong (150°) sulphuric acid for a Deacon unit is about five or six tons per 24 hours in summer, and rather less in winter. Too great economy in that respect would injure the quality of the bleaching-powder.

By thorough drying Worsley, Windus, and Bracey (Eng. pat. 16151, 1893) prepare Deacon chlorine even for condensation to the *liquid* state by strong compression, for which purpose they describe a special apparatus.

*7. Absorption of the Chlorine by Lime.*—The chlorine gas, purified from hydrochloric acid and water, is always so much diluted by nitrogen and an excess of oxygen that its absorption in ordinary bleaching-powder chambers is not at all feasible. It mostly contains 5 to 7 per cent. Cl and 93 to 95 per cent. air. Indeed the bulkiness of the volume of the gases to be dealt with here presents a great difficulty; it amounts to about 20,000 cubic feet per ton of saltcake. Such a quantity of gas can only be dealt with by continuous absorption by being drawn away as it is formed and completely deprived of chlorine in its passage through the absorbing-apparatus. In order to do this, Deacon employs the hydrated lime in a very thin layer (not above  $\frac{1}{8}$  inch), in a series of large *chambers* made of slate or sandstone flags, containing each a number of horizontal shelves at distances of 6 inches from each other. Figs. 137 and 138 show a front elevation and two sectional elevations of the chambers. In these the gas must pass over a very large surface of lime. By convenient cast-iron distributing-pipes each chamber can be made the first or the last with respect to the current of gas. The gas coming from the drying-apparatus, comparatively rich in chlorine, is passed through the oldest chamber, in which the lime is nearly saturated; at the end of the set the nearly exhausted gas meets with fresh calcium hydrate and gives off its chlorine to this so completely that often the gas issuing from the Roots' blower cannot be smelt at all.

Fig. 137.

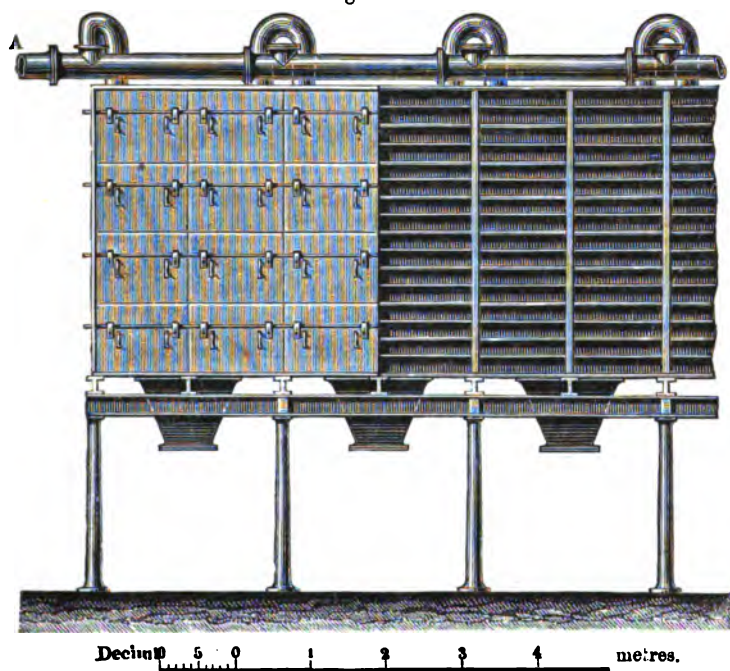
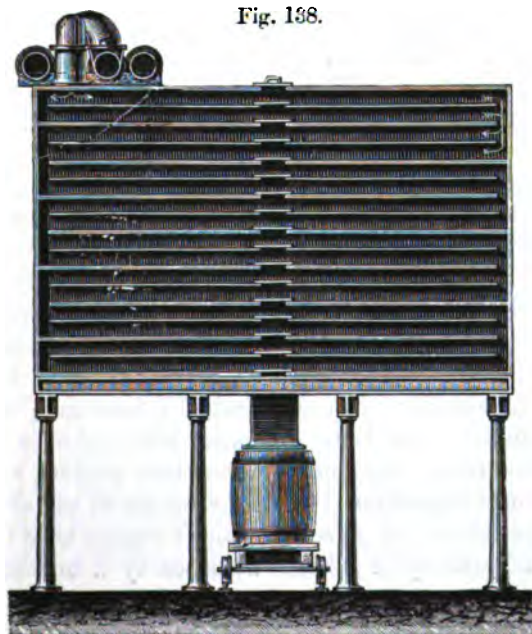


Fig. 138.



The first chamber, when it has been completely saturated, is cut off, emptied, charged with fresh lime, and made the last chamber, the fresh gas being moved forward to the next chamber. In this way Deacon has certainly overcome the difficulty of managing such a large bulk of gas; but the first cost of his chambers is enormously high, as they must be built of expensive material and rest on a most substantial foundation; any settling instantly produces a leakage of air inwards through the joints. Another plan proposed by Deacon (pat. No. 691, 1871), but not successfully carried out, was, to have a tower with slanting slate shelves inclined alternately in different directions, the bleaching-powder gradually sliding down upon these by the assistance of a shaft and blades, fresh lime being put in continuously at the top, and finished bleach drawn out at the bottom. The principle of this apparatus is exactly the same as that of Leather, patented for ordinary bleach (see below).

Hurter has published an extensive investigation (Dingler's Journal, ccxxiii. p. 417; ccxxiv. p. 424) of the progress of the absorption of the chlorine by calcium hydrate, the disturbing effects of the foreign gases mixed with the chlorine, and the influence of the heat given off during absorption. Its results are as follows:—The depth of the layer of lime has no influence upon the absorption, but the chlorine simply penetrates down to the same depth in equal times. The lime, being a very fine porous powder, of specific gravity 0.5 (including the air), can be but slowly penetrated by chlorine, because the occluded air cannot escape instantaneously. Thus a slow current is formed, all the slower the more deeply the gas has to penetrate. The absorbing-capacity of the whole absorbent layer when its surface is already covered with finished bleach is only half as much as that of fresh lime. In the beginning of the absorption, but only for a very short period, instantaneous absorption will go on very quickly; then the absorbing capacity falls to about one half and remains constant till the chlorine meets with the last layer of lime; from this point the absorbing capacity gradually decreases; and at last, when all the lime has been saturated with chlorine as far as possible, it is zero. The middle period lasts longest, and is practically the most important. On the strength of the above theory and of experiments on a small scale, formulæ have been calculated for the quantity of chlorine absorbed by a unit of space for

any given time; and practical experience on a large scale has justified the correctness of those formulæ. The depth of lime allowable was calculated according to them by Hurter at 1.61 centim.; this must be considered the maximum for practical work, for which  $\frac{5}{8}$  inch (=1.5 cm.) had previously been stated. The dimensions of the chambers could also be calculated in this way. In order to finish 25 tons of bleaching-powder per week, considering that the lime takes 96 hours to be converted into bleach, at least four chambers must be provided for working, and one for emptying and recharging, if one chamber is to be finished daily. Consequently each set must consist of at least five chambers, each of which must hold as much lime as corresponds to  $4\frac{1}{6}$  tons of bleach. As this would be an enormous area, the chambers have been made to come on turn every 16 hours. In order to save connecting-pipes, the gas is conveyed in one chamber from the upper to the lower shelves, in the next from the bottom to the top; each two such compartments form a pair of chambers to be laid off at a time. Of such pairs  $\frac{96}{16}=6$  are required for working, and one more for charging. Indeed Deacon's chamber-set consists of seven pairs with 16 shelves each, on the whole  $7 \times 2 \times 16=224$  shelves. The 16 shelves of each chamber have an area of 1250 square feet, upon which  $18\frac{1}{2}$  cwt. of calcium hydrate can be laid  $\frac{5}{8}$  inch deep. Since in a week of 6 days  $\frac{144}{16}=9$  pairs of chambers are drawn, this means  $2 \times 9 \times 18\frac{1}{2}$  cwt.=16 tons 13 cwt. slaked lime, which furnish 25 tons of bleach. With good works and higher tension of gas [which but very rarely exists in practice] Hurter's theory and practice yield much more (as much as 33 tons of bleach per week from a Déacon's chamber-set), but with a lower tension of gas considerably less. [The average area of Deacon chambers, according to the 19th Alkali Inspector's Report, p. 29, is certainly much in excess of that stated by Hurter, viz. 1373 superficial feet per ton of bleach per week.]

Since the slate or sandstone chambers do not conduct the heat liberated in the formation of bleaching-powder (according to Hurter 195 units of heat to each unit of weight of bleach) so quickly as the lead or iron chambers of the ordinary process, and since in them the process of absorption is even greatly intensified by the large number of shelves, which do not radiate any heat

outwards, it would not be possible to employ strong chlorine gas in Deacon's chambers, as the temperature in them would otherwise rise to 70° or 80° C. Hence the chlorine must always be to some extent diluted with inert gases, which in practice is always sufficiently the case.

That it is more advantageous to convey the gas in the absorbing-apparatus in a downward than in an upward direction Hurter had already shown, in a paper treating of the Hargreaves process (Dingl. Journ. ccxxiii. p. 200).

Schäppi (Fischer's Jahresb. 1882, p. 379) states that in England the *lime* is slaked to the point where it is just possible to pass it through a sieve, and that it then contains from 24.5 to 27 per cent.  $H_2O$ . But at well-conducted works such wide limits of the percentage of water ought not to be permitted !

The proper *temperature* of the gas is to be produced, according to Hurter's patent No. 7393, 1892, by employing during the hot season previously cooled sulphuric acid in the drying-tower, and in case of need surrounding the gas-pipe leading to the chambers by artificially cooled brine. If, on the other hand, the gas is too cold, it is to be heated in the drying-tower by tepid sulphuric acid and by a hot-water jacket round the gas-pipes.

Muspratt, Carey, and Driffield (Engl. pat. No. 1214, 1893) carry off the heat produced in the absorbing-chambers by conducting the gas from one compartment to the other through connecting-pipes cooled with water, or, if sufficiently long, by air. Another patent, by Gaskell, Driffield, Carey, and Wright (No. 25023, 1893), further employs coke-towers fed with sulphuric acid, in which the gas is first dried as it comes from any one of the compartments; it then passes through the just-mentioned coolers, and subsequently into the next compartment.

Hargreaves, Robinson, and Hargreaves (pat. No. 5673, 1886) convey the weak Deacon chlorine only on to the upper shelves of the absorbing-apparatus, while the lower shelves receive strong chlorine, generated as described on p. 398. The weak bleaching-powder obtained on the top is turned over on the lower shelves and is brought up to proper strength by the strong chlorine, whereupon it is transferred by agitating apparatus into an air-tight box, from which it is removed by mechanical means into casks and automatically pressed down.

Instead of the very large and expensive Deacon-chambers,

recently *mechanical* chlorine-absorbers are said to have been employed, which we shall describe in the chapter treating of bleaching-powder.

8. The *draught* in the whole Deacon apparatus is produced by *aspirating-apparatus* of suitable kind. In England they employ in this case the well-known Roots' blower (described Vol. II. p. 264). Elsewhere, possibly now also in England, Körting's injectors are employed.

Formerly the work was performed under greater minus-pressure than at a later period. After it had been recognized that damage was done by the entrance of fuel-gases containing carbonic acid through the joints of the superheater and of the decomposer (see below), the suction at the end of the apparatus was diminished as much as possible. Schäppi (Fischer's Jahresb. 1882, p. 379) states that the inward draught, which had been previously equal to a column of water of 20 to 40 centimetres, had been subsequently diminished to 2 centimetres. But this statement is not of much value, as the inward draught must be very different at different places of the long series of apparatus from the saltcake-pans to the bleach-chambers, and variations like those noticed by Schäppi produce quite an erroneous impression if the readings are not always made at the same place. At all events he is wrong in stating that in the case of leaks the chlorine gas would more readily go into the chimney than fuel-gases would enter into the decomposer, for, as we have seen, p. 401, there is *everywhere* an *inward* draught, and the entrance of fuel-gas can be prevented only by an air-tight construction of the parts exposed to the fire.

A great drawback of the Deacon process was for a long time found in the circumstance that the bleaching-powder frequently came out *too weak*. Some manufacturers never got beyond this stage; and the majority, who at first obtained very good bleach, found that it gradually became weaker and weaker. Sometimes the redipping of the marbles remedied the mischief; but often it did not. The chief cause of the production of weak bleach was found to be the difficulty of keeping the apparatus completely tight. Just that peculiarity of the process which in some respects is one of its greatest advantages acts injuriously here, viz., the fact that in the apparatus there is a lower pressure than outside, so that no nuisance can be caused by chlorine escaping; for this facilitates the entrance of air through any leakages in the numberless joints

of iron and stoneware or glass pipes, the many-shelved absorbing-chambers, &c. Most damage is done by the entrance of fire-gases containing *carbonic acid* into the heating-apparatus and the decomposer, as that gas is greedily absorbed by the lime in the chambers. The influence of the foreign gases, especially  $\text{CO}_2$ , was minutely investigated by Hurter in the above-cited paper (p. 406). In the manufacture of bleach from native manganese ore or by the Weldon process,  $\text{CO}_2$  very rarely occurs in such quantity as to prevent the manufacture of bleach containing 40 Cl per cent. But in the Deacon process it is different: for a ton of bleach 70,000 cubic feet of air are needed—that is, only about one third of the quantity required in the Weldon process; but its  $\text{CO}_2$  is greatly increased on its long path through the superheater and decomposer, which are surrounded by fire-gases. The former is easily kept tight, but the latter only with very great care. In the shape employed at first, where the decomposer consisted of a square cast-iron box, the joints of the plates must open on cooling. Even if at starting a working-period all the joints have been made perfectly tight, they cannot fail to be opened by any variations of temperature during the work; for in heating up, the volume of the apparatus increases; the marbles slide down, and offer an insurmountable obstacle to the closing-up of the metal plates when they contract on cooling. With very great care an apparatus can be kept sufficiently tight for a whole year. It is never absolutely tight; but this does no harm, so long as the total surface of all the leaks together does not amount to more than 1.5 square centimetre. The situation of a leak can rarely be discovered during work; and still more rarely can it be put right without stopping the apparatus. Thus, for instance, it was found that 10,000 vols. of the gas on entering the heating-oven contained 5 vols.  $\text{CO}_2$ , on entering the decomposer 19 vols., on leaving the same 38.5 vols., and the bleach could not be made above 32 per cent. This source of carbonic acid, if it once exists, is the only one which is not under control. Hurter convinced himself, by direct experiments, that from a mixture of carbon dioxide and chlorine calcium hydrate absorbs the former by preference, because  $\text{CO}_2$  decomposes bleaching-powder; and when the top layer of lime has long ceased to absorb chlorine, it still absorbs  $\text{CO}_2$ . Hence in Deacon's chamber weaker bleach is always formed at the place where the gases enter, and accordingly throughout the first chamber.



Various changes in the shape of the decomposer have been tried for the purpose of remedying this defect; and by making the decomposer cylindrical the occurrence of weak bleach has been altogether avoided.

Another source of weak bleach has been pointed out, viz. the *arsenic* in the sulphuric acid, both in that employed for decomposing the salt and in that employed for drying the chlorine. That arsenic exercises a disturbing influence on the activity of the copper-salt had been maintained previously (comp. p. 397); it was recognized later on that the arsenious acid, or the  $\text{AsCl}_3$ , after the chlorine has been evolved, is oxidized very gradually, with formation of hydrochloric acid, according to the equation



Perhaps not  $\text{AsCl}_3$ , but a solution of  $\text{As}_2\text{O}_5$  in  $\text{HCl}$  is formed. This would appear to be very probable from a fact observed by Dr. Hewitt and Mr. Davis at the Radcliffe chemical works. There the  $\text{HCl}$  is washed out of the mixed gases by means of a coke-tower for strong acid and a post-condenser; the washings running off from the latter mark nothing on the hydrometer and taste hardly acid. In spite of this, in the string of pipes leading from the post-condenser to the drying-tower a solution of arsenic acid of spec. grav. 1.070, and in the pipes leading away from the drying-tower a solution of  $\text{As}_2\text{O}_5$  in  $\text{HCl}$  of the consistency of treacle are condensed. It is asserted that the arsenic can be traced even to the bleaching-powder chambers; and to this gradual formation of  $\text{HCl}$  is ascribed the largest share in the production of weak bleach. Endeavours have been made to remedy this mischief by purifying the sulphuric acid from arsenic by heating it with common salt: the  $\text{AsCl}_3$  volatilizes almost completely; and the  $\text{HCl}$  coming afterwards is nearly free from it. But this process would have to be applied not merely to the sulphuric acid of the drying-tower, but also to that employed in the saltcake-pans; and in that case it is just the strongest acid gas which could not be employed for the Deacon process. It is therefore very doubtful whether this process is economically feasible; and for the same reason the employment of sulphuric acid purified by sulphuretted hydrogen &c., or made from Sicilian brimstone, is probably out of the question. After all, it would remain to be seen whether by employing sulphuric acid free from

arsenic strong bleach would be *regularly* obtained. According to reports received in 1879, the expected success had not been obtained ; but at the present day not so much stress is laid upon the alleged injurious action of the arsenic (p. 396).

According to Schäppi (Fischer's Jahresb. 1882, p. 379), if the decomposition reaches 50 per cent., the bleaching-powder is always strong and tests from 34 to 37·5 per cent. in the casks ; the average of the hottest months is 35 to 35·5, in winter 36 per cent. Since stronger sulphuric acid has been employed for drying (150° Tw. ; comp. p. 408), the bleach is always strong ; but the draught must also be good, so that there is at least 4 vols. air to 1 vol. HCl, since otherwise the decomposition is bad, the washing apparatus is no longer sufficient for the work imposed upon it, and HCl gets into the bleaching-powder. Too much draught does much less harm than too little in this respect. Schäppi states that it has been attempted to make Deacon chlorine stronger by mixing Weldon chlorine with it, but this did not succeed ; the bleaching-powder went into a paste ; it contained much chlorate, and sometimes flowed out of the chamber doors. [This mishap has decidedly only occurred under very exceptional circumstances, and no fear of it need be entertained when using proper precautions !]

If Deacon chlorine is to be employed for manufacturing *bleaching-liquor* (liquid chloride of lime), any not excessive admixture of CO<sub>2</sub> does little damage, and this is still less the case when employing it for the manufacture of *chlorate of potash or soda*, when chlorate of lime is first produced. This was indeed one of the first cases in which the Deacon process obtained a permanent hold.

It should not be overlooked that Deacon chlorine is never free from traces of *copper*. This is probably quite harmless in the manufacture of bleaching-powder and chlorates, but it might interfere with its direct use in some other chemical processes.

*Results of work.*—I must confess that the above given description of the Deacon process and of the plant employed will not satisfy all expectations. The apparatus, as first constructed, acted very imperfectly and the success of the process was correspondingly small. At first, on account of its undeniable superiority, it was very quickly introduced, at least in England. But the

great drawbacks existing during its early stage soon led to a retrograde movement. Of twelve plants erected in England since 1871, only four were at work in 1878 and three in 1879. But in these, as well as in the two works erected in Germany (Rhenania and Kunheim's), continual efforts were made at improving the process, undoubtedly to a great extent by modifications of details which could not very well be patented and which on that account were kept strictly secret. Later on one or two plants were erected in France. Since the original patent had lapsed, Deacon's firm had no more interest in introducing the process, which further contributed to the secrecy in which all improvements were kept. Probably the various factories now employ apparatus similar in principal to those above described, but differing in details from them and among each other. There is no question that for a number of years the Deacon process has been in regular, successful work at a good many places, and that it furnishes chlorine much more cheaply than the Weldon process, although in a dilute state. Whereas the Weldon process requires for 20 cwt. bleach at best 45 cwt. of salt (p. 365), that quantity of bleach by the Deacon process is obtained from 32 to 40 cwt. of salt, if only the pan-gas is used, together with 10 per cent. of the pan-acid and all the roaster-acid, which can be used for the Weldon process, or worked up by the Hasenclever process &c., or else sold. By combining the Deacon and Hasenclever processes, a ton of bleach can be made from 15 cwt. of salt (Alkali Inspectors' Report for 1892, p. 66).

In spite of the great and indubitable advantages of the Deacon process, it is a fact that even in 1895 by far the greatest part of the bleaching-powder made in England was produced by the Weldon process. Perhaps this is explained by the fact that enough acid was yielded by the Leblanc works to produce all the bleaching-powder required by the Weldon process, and that, therefore, manufacturers shrank from investing a large amount of capital in Deacon plant; but I cannot myself accept this explanation as sufficient.

The *wages* for the Deacon process—slaking the lime, charging the chambers, packing the bleach, firing the superheater and decomposer, dipping the marbles, and general superintendence—are stated by Schäppi=14*s.* or 15*s.* per ton; to this must be added 1*s.* for copper. [The last item must depend on the price of copper.]

The consumption of *coals* is very slight for the Roots' blower, and not very large for the superheater, so that it need not exceed in all 8 or 10 cwt. per ton of bleach.

We must not overlook the advantage that no nuisance can be caused in the neighbourhood of works by this process, since neither HCl nor chlorine can escape through the leaks, owing to the inward draughts.

The Chemical Trade Journal, 1890, vol. vi. p. 16, contains a cost-sheet evidently drawn up by a well-informed person. At the factory in question a ton of bleach was made from 30 cwt. hydrochloric acid, only the pan-acid being employed. The most favourable work was, in decomposing 30 tons per week (of 132 hours), a yield of 21 tons of bleach, with a consumption of 23 cwt. copper ashes for 1000 tons of bleach. The exact costs per ton of bleach were :—

	£	s.	d.
Wages .....	0	15	1
Coals (at 6s.) .....	0	2	8
Lime.....	0	7	0
Copper ashes .....	0	1	2
Casks .....	0	13	0
Repairs... ..	0	4	0
Depreciation .....	1	13	4
General expenses.....	0	13	4
Acid .....	0	10	5
	<hr/>		
	£5	0	0

[The following remarks must be made with reference to these statements, taken from an actual case. The very high amount set down for depreciation corresponds to 10 per cent. on a cost of plant = £13,000, and is calculated on the actual weekly average make of not quite 16 tons of bleach. Other manufacturers assert that they have erected a Deacon "unit" at much less cost and with a much larger turn-out, which must strongly influence the figure for depreciation, and probably also that for repairs. The general expenses are also very high in the case in question. On the other hand, the sum of 10s. 5d. for "acid" seems very low indeed, and at most places much more than that will be put in the cost-account, even when utilizing the re-condensed acid as much as

practicable. The present costs of Deacon bleach, which in England is now exclusively made by the United Alkali Company, are kept strictly secret, and information is refused even as to the quantity manufactured by this process.]

The *cost of plant* for a Deacon "unit" was stated in the years after 1870 at a minimum of £8000, but they were sometimes twice as high, for a weekly make of 20 to 22 tons of bleach. Especially the bleach-chambers were very expensive; this is one of the reasons why the process was from the first regarded in a more favourable light for the manufacture of chlorates. What the cost at the present day would be I do not know. Kolb (Rev. Chim. Industr. 1892, p. 165) says that it does not cost much more than a Weldon plant, and requires less repairs, labour, and wages. The Chemical Trade Journal, quoted above, states it, for 1890, = £13,000. This does not include the plant for the Hasenclever process.

## CHAPTER XIX.

PROPERTIES AND BEHAVIOUR OF THE HYPOCHLORITES  
AND OF BLEACHING-POWDER.

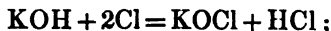
THE affinity of chlorine for oxygen is very slight; they cannot be directly combined. Indirectly, however, a number of compounds of chlorine with oxygen only (anhydrides) and with both oxygen and hydrogen (the acids of chlorine) are obtainable. Of these we are at present only interested in *hypochlorous acid*,  $\text{ClOH}$ , and its anhydride  $\text{ClOCl}$ . Chlorine yields hypochlorites with aqueous solutions of the alkalis and alkaline earths, or with their hydrates containing a little water. When chlorine is not in excess, chloride and hypochlorite are formed from the alkaline hydrates; with an excess of chlorine, chloride and free hydrochlorous acid are obtained—the former in accordance with the equation



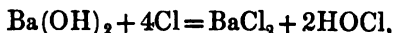
the latter according to



Blomstrand (Gmelin-Kraut, i. 2, p. 353) states that at first hypochlorite and hydrochloric acid are formed:



the  $\text{HCl}$  then saturates a second molecule of potash. According to Williamson (*ib.*), caustic potash-liquor, on being supersaturated with chlorine and shaken in the air, absorbs  $1\frac{1}{2}$  eq. chlorine; the bleaching-liquid contains *no* salt of hypochlorous acid, but already chloric acid or potassium chlorate. Baryta-water, saturated with chlorine and shaken with air, absorbs 4 eq. chlorine, and then contains barium chloride and free hypochlorous acid,

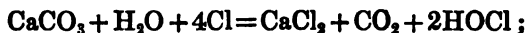


but no barium hypochlorite, since  $\text{CO}_2$  does not cause a precipitate, and silver nitrate yields a white precipitate, not, as with hypochlorites, a black one. Hence the hypochlorite at first produced must be completely decomposed by further chlorine :



According to Konigel-Weisberg (Ber. d. deutsch. chem. Ges. xii. pp. 346, 511), dry barium hydrate is not affected by chlorine. In the presence of water, one molecule of  $\text{BaO}$  will absorb two molecules of  $\text{Cl}$ . Any hypochlorite at first formed decomposes quickly into chlorate and chloride, which two form the final products. Strontia behaves exactly in the same way. The action of chlorine on calcium hydrate is more complicated, and will be subsequently explained in connexion with bleaching-powder.

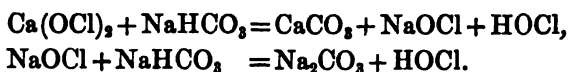
If chlorine is passed through water in which finely powdered chalk is suspended, the latter is dissolved as  $\text{CaCl}_2$ ,  $\text{CO}_2$  escaping and aqueous  $\text{HOCl}$  being formed, which can be distilled off (Williamson ; Kolb : the equation should be



but under such circumstances hypochlorous acid is quickly transformed into chloric acid). Chlorine passed into a solution of an alkaline carbonate produces chloride along with free  $\text{HOCl}$  according to some authors, or hypochlorite according to others. Hypochlorous acid can in no case expel  $\text{CO}_2$  from carbonates, except by its own decomposition, and hence does not cause any effervescence in a solution of sodium carbonate [this is contradicted by Walters, Wagner's Jahresb. 1874, p. 847] or any precipitation of bicarbonate ; in the presence of alkaline carbonates it retains its smell and its bleaching-property. If only just too little chlorine is passed through a solution of  $\text{Na}_2\text{CO}_3$  to produce any effervescence, a pale yellow liquid is obtained, smelling faintly of chlorine, by which turmeric-paper is first reddened and then bleached ; it loses scarcely any of its bleaching-power on boiling, but much on evaporation to dryness ; and the quicker the evaporation the greater the loss. If a solution of  $\text{Na}_2\text{CO}_3$  be supersaturated with chlorine, a yellow, strongly bleaching liquor is obtained, which, when evaporated in a thin layer in warm air, leaves a residue by which turmeric is first turned brown and then decolorized, which therefore, in spite of the

excess of chlorine, still contains sodium carbonate. On boiling, this liquid evolves chlorine, loses its colour, and leaves on evaporation sodium chloride, chlorate, and a little carbonate (Gmelin-Kraut, *l. c.*).

Austen (Chem. Zg. 1889, Rep. 115) states that bleaching-powder solution reacts with sodium bicarbonate as follows :



We have thus a free mineral acid in an alkaline solution. On boiling, hypochlorous acid decomposes into HCl and O; the former decomposes  $\text{Na}_2\text{CO}_3$ , so that the escaping gases form a mixture of  $\text{CO}_2$  and O. On boiling a solution of sodium hypochlorite no oxygen escapes, but this takes place if  $\text{CO}_2$  had been previously passed through the solution.

According to Phipson (Compt. Rend. lxxxvi. p. 1196), hydrogen-sulphide acts on bleaching-powder in this way, that the smell of the former vanishes and an odour of chlorine is perceptible; free sulphur becomes visible. Probably at first hypochlorous acid is formed, which reacts with  $\text{H}_2\text{S}$ , liberating Cl and S.

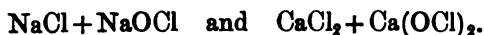
The anhydride of hypochlorous acid,  $\text{Cl}_2\text{O}$ , is a blood-red liquid, of powerful chlorine-like smell, boils at  $19^\circ\text{--}20^\circ\text{C}$ ., and is easily decomposed even at ordinary temperatures, often with an explosion. Water at  $0^\circ\text{C}$ . absorbs more than 200 vols. of the gas, the hydrate:  $\text{ClOH}$  being formed. The aqueous acid can be made, as mentioned, by passing chlorine gas into chalk suspended in water and distilling, or by shaking chlorine gas with mercuric oxide suspended in water, or by incompletely saturating bleaching-powder with very dilute nitric acid and distilling. The concentrated aqueous acid has the smell of the gas and a strong taste, and a highly caustic action on the skin. In the air it volatilizes almost entirely. The concentrated acid, on being heated, gives off a reddish-yellow gas; the diluted acid at  $100^\circ\text{C}$ . only a little gas, but much more on adding calcium nitrate or phosphoric acid: concentrated sulphuric acid decomposes it into chlorine, hypochloric acid, and a little oxygen. The dilute acid decomposes slowly even in the dark, and the more quickly the more concentrated and hot it is; concentrated acid will keep only for a few days, even if surrounded by ice; it yields chlorine and chloric acid. In daylight the decomposition proceeds more rapidly. The dilute acid can be concentrated by



fractional distillation, the stronger acid passing over first; but here also chlorine, oxygen, and chloric acid are formed, especially from the concentrated acid.

The solution of hypochlorous acid is a very powerful oxidizing agent, dissolving many metals up to the maximum of their oxygenation or chlorination; it also decomposes many organic compounds.

The *Hypochlorites* of the alkaline metals, of magnesium, zinc, and copper, can be obtained by mixing the hydroxides with dilute  $\text{ClOH}$ . The solutions, when containing carbonate in excess, can be dried down at the ordinary temperature *in vacuo* without decomposition. Much more frequently hypochlorites are obtained mixed with chlorides by admitting no more than an equivalent of chlorine to the aqueous solution or suspension of the alkalis, alkaline earths, or magnesia at a low temperature. Too high a temperature or an excess of chlorine causes decomposition (see above). Formerly the solutions thus obtained were believed to contain direct compounds of chlorine with the alkalis &c.—*e. g.*  $\text{Na}_2\text{OCl}_2$ ,  $\text{CaOCl}_2$ . Berzelius already in 1808 pronounced them to be mixtures of a chloride and a salt of an acid of chlorine; and since Balard's discovery of hypochlorous acid they are generally regarded as mixtures of chlorides and hypochlorites—*e. g.*



With *solid* chloride of lime the case is different, as we shall see.

The hypochlorites,  $\text{MOCl}$ , have a caustic and astringent taste; they do not produce any white spots on the skin, and in contact with organic substances have a peculiar faint smell. That their smell is not attributable to free hypochlorous acid, as usually assumed, we shall see later on. In the dark at the ordinary temperature they give off oxygen very slowly; in daylight (and much more quickly in sunlight) the solutions of the alkaline hypochlorites decompose into chloride, chlorite, and chlorate, with evolution of oxygen. A solution of chloride of lime, when kept in a closed vessel, gradually gives off oxygen, especially in daylight, and leaves  $\text{CaCl}_2$  behind; in direct sunlight chlorite also is formed, along with a little chlorate. On heating the aqueous solution, even *in vacuo*, if the alkali does not greatly predominate, the alkaline hypochlorites are decomposed, mostly with evolution of oxygen, into chloride and chlorate. But with an excess of alkali, alkaline

hypochlorites can be evaporated even at 50° C. without decomposing into chloride and chlorate; the residue still bleaches strongly. Solutions of chloride of lime are by long-continued boiling converted into calcium chloride and chlorate: during this no oxygen escapes if the solution contained only 16 grams  $\text{CaO}_2\text{Cl}_2$  per litre; but from solutions containing 22, 32, and 48 grams  $\text{CaO}_2\text{Cl}_2$  per litre only 80.5, 48.4, and 43.8 per cent.  $\text{Ca}(\text{ClO}_3)_2$  are obtained, because oxygen is lost (Schlieper, Ann. Chem. Pharm. c. p. 171). Gay-Lussac and Mitscherlich already noticed that the evolution of oxygen on boiling solutions of bleaching-powder was increased by the addition of powdered manganese, ferric oxide, cupric oxide, &c., without these substances themselves being decomposed. Fleitmann (Ann. Chem. Pharm. cxxxiv. p. 64) observed that concentrated solutions of bleaching-powder are completely decomposed into calcium chloride and oxygen on being heated with a trace of cobalt peroxide; and this reaction has often been employed for making oxygen. Several other substances act in the same way (Gmelin-Kraut, i. 2, p. 359).

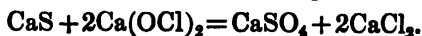
The action of an excess of chlorine on hypochlorites at the ordinary temperature is of practical importance. By this free hypochlorous acid is obtained, *e.g.*



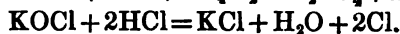
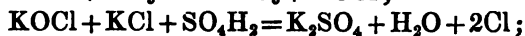
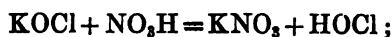
Bleaching-powder also behaves in this way; and the presence of free hypochlorous acid can be proved by distillation. In this case, even at the ordinary temperature, according to Baillard chlorate is formed, but according to Martens and Kolb very little or none (comp. my own researches in the chapter treating of Chlorates). It is established, however, that the conversion of hypochlorites into chlorate by heating is very much hastened by the presence of an excess of chlorine; and since, under such circumstances, where by an excess of chlorine free hypochlorous acid is formed a rise of temperature can hardly be avoided, there is nearly always a noticeable, and sometimes a predominant formation of chloric acid.

The hypochlorites act as oxidizers in the same way as the free acid, and raise most of the lower oxides to the highest degree of oxidation. They destroy organic colouring-matters and smells (*i. e.* they bleach and disinfect), though only slowly and to a small extent when other acids are entirely excluded. The hypochlorites,

however, may exert an oxidizing and consequently a bleaching action even without HOCl or Cl becoming free: *e. g.*



It is indeed possible to bleach fabrics or paper-pulp completely in closed vessels in the absence of air; but certainly the oxidizing and bleaching action of hypochlorites takes place much more readily with the assistance of acids, even of the weakest: carbonic acid, for instance, causes a strong action of this kind, as, like the other acids, it sets hypochlorous acid free. When  $\text{CO}_2$  acts upon dissolved or moistened bleaching-powder, the HOCl becomes free and all the lime combined with it is precipitated as carbonate. An insufficient quantity of sulphuric or nitric acid also causes the liberation of hypochlorous acid from hypochlorites; but hydrochloric acid, or an acid decomposing chlorides with separation of HCl, yields both chlorine and free hypochlorous acid; and of course the same thing happens when from the first a sufficient excess of strong acid is added:



[The above statements on the reactions of hypochlorous acid and its salts, chiefly taken from Gmelin-Kraut, must be supplemented by the researches of the last few years, mentioned below.]

The action of ammonium chloride upon bleaching-powder has been studied by Salzer (Dingl. Journ. ccxxx. p. 418). The two substances, shaken together in the dry state, give off an explosive gas, probably by the decomposition of ammonium hypochlorite. Pure and saturated bleaching-powder (38 per cent. chlorine) does not yield any free ammonia with ammonium chloride if dry, but only after it has become moist; this seems to prove that no free lime is present. After trituring such bleaching-powder with 100 times its weight of water and adding a neutral solution of ammonium chloride in excess, a perfectly clear, neutral, not bleaching liquid is formed, which gradually gives off gas and turns acid.

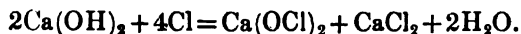
The only hypochlorite obtained in a *crystallized* state is that of calcium, described by Kingzett (Chem. News, xxxi. p. 113; xxxii. p. 21). He caused a filtered solution of bleaching-powder to freeze in a refrigerating-mixture, and allowed the solid mass obtained to thaw on a filter, by which he obtained feathery crystals almost an

inch long; he also obtained the crystals by allowing the solution to stand in a vacuum beside sulphuric acid or caustic potash. They are very unstable, and in the air lose chlorine or hypochlorous acid. According to Kingzett's analyses they are  $\text{Ca}(\text{OCl})_2 + 4\text{H}_2\text{O}$ ; but those analyses are not sufficiently concordant to make certain the exactness of that formula. The "crystallized calcium hypochlorite" must therefore be examined further before its existence can be pronounced indubitable. Kingzett points out that this product has the great advantage over bleaching-powder of being entirely soluble in water and containing the bleaching chlorine in a much smaller volume. But these advantages are of very little moment, looking at the extremely slight stability of the salt; and, moreover, its discoverer himself says he is unable to indicate a technically available process for its production.

#### *Chloride of Lime (Bleaching-Powder).*

We have already mentioned this product several times, but have almost exclusively described the reactions of its solution, in which, almost universally, calcium hypochlorite is assumed to be present along with calcium chloride; and the product obtained by absorption of chlorine in milk of lime (bleach-liquor) behaves in just the same way; but the product obtained by absorption of chlorine by slaked lime, the bleaching-powder itself, must be submitted to a special consideration, since opinions widely differ as to its constitution.

At first and for some time after the discovery of bleaching-powder it was assumed to be simply a compound of chlorine and lime, according to modern atomic weights  $= \text{CaOCl}_2$ . Balard in 1835 (*Ann. Chim. Phys.* [2] lvii. p. 225), after discovering hypochlorous acid and studying the alkaline hypochlorites, came to the conviction that bleaching-powder is a compound or mixture of equivalent proportions of calcium hypochlorite and chloride  $= \text{CaO}_2\text{Cl}_2 + \text{CaCl}_2$ , mixed with an excess of calcium hydrate. In a research of Gay-Lussac's in 1842 (*ib.* [3] v. p. 273) Balard's formula was confirmed by new arguments; and for many years it was almost universally assumed that not merely the solution, but also solid bleaching-powder was explained by the simple formula

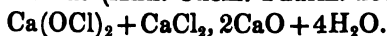


But this opinion was shaken by two facts which could not be

long overlooked, viz. :—1st, that the presence of free calcium chloride in bleaching-powder is nothing like so clearly evidenced (by its deliquescence, solubility in alcohol, &c.) as the above formula requires; and, 2nd, that the formula does not explain the notorious fact that solid bleaching-powder is not obtainable without a large quantity of free calcium hydrate. This caused a number of other formulæ to be proposed.

These and many subsequent investigations are discussed at length in our first edition, Vol. III. pp. 92–106. Here we merely allude to this subject, as those papers have merely an historic interest now, since it has been shown that bleaching-powder can be made with considerably less free calcium hydrate than is required by any of those formulæ, and that this free calcium hydrate escapes chlorination merely in a mechanical way, by being encrusted with the proper bleaching compound, as had been contended by Bolley as early as 1859. We shall therefore only quote, without further discussion, a few of those formulæ, proposed on the ground of the presence of free lime :—

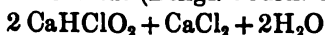
Fresenius (Ann. Chem. Pharm. xcvi. p. 317) :



Kolb (Compt. Rend. lxx. p. 530) :



Stahlschmidt (Dingl. Journ. ccxi. pp. 243 & 335) :



(his structural formula for  $\text{CaHClO}_2$  is:  $\text{Ca} \begin{array}{c} \text{—OH} \\ \text{—OCl} \end{array}$ ).

In opposition to this, many chemists even then maintained the formula  $\text{CaOCl}_2$ , but they interpreted it differently, *e.g.* Millon and Muspratt:  $\text{Ca} \begin{array}{c} \text{—O} \\ \text{—Cl}_2 \end{array}$ ; Odling (in his 'Handbook of Chemistry,' but without giving any reasons for it):  $\text{Ca} \begin{array}{c} \text{—Cl} \\ \text{—OCl} \end{array}$ ; Goepner (Dingl. Journ. ccix. p. 204) :  $(\text{CaO})\text{Cl}_2$ ; similarly Richters and Juncker (Dingl. Journ. ccxi. p. 31), and Walters (Journ. f. prakt. Ch. [2] x. p. 128), who contends that even a solution of bleaching-powder at first contains  $\text{CaOCl}_2$ , not a mixture of hypochlorite and chloride. This is approved by Opl (Dingl. Journ. ccxv. p. 83). O'Shea (Journ. Chem. Soc. xliii. p. 410) agrees with Odling's formula.

Extensive investigations on bleaching-powder and its constitution have been made by myself in conjunction with several of

my students, of which a very brief summary will now be given. Lunge and Schäppi (Dingl. Journ. ccxxvii. p. 63, and Chem. Ind. 1881, p. 289) found that perfectly dry chlorine acts already on lime containing only 6.5 per cent. water, and thereby yields a product containing 9.06 per cent. available chlorine. The capacity of lime for absorbing chlorine increases with its percentage of water; at 24.0 per cent.  $H_2O$  we obtained bleaching-powder with 40.71 per cent., at 27.8 per cent.  $H_2O$  it contained 43.13 or 43.42 per cent. available chlorine. If the percentage of water increases further, the percentage of available chlorine slowly decreases; but even at 31.8 per cent.  $H_2O$  in the lime, still 36.85 per cent. available chlorine is reached. Moist chlorine, passed over dry calcium hydrate (with about 24 per cent.  $H_2O$ ), yields good bleaching-powder with 38 to 42 per cent. chlorine. The strongest bleach is always obtained if the total moisture of the chlorine and the lime (calculating the excess of water over the 24.3 per cent. required for forming the hydrate) is about 4 per cent. That is: with perfectly dry chlorine the lime should contain about 28 per cent., but less than that with moist chlorine. [In fact at Aussig they keep the percentage of water in the lime during summer = 24.5 or 25 per cent.; during winter, when more moisture is condensed in the 200 feet of piping through which the chlorine is conveyed, they put the lime into the chambers with 25.5 per cent.  $H_2O$ , and this is checked by daily tests. We at the same time drew attention to the advantage, since then re-discovered and patented, of employing perfectly dry chlorine and also exactly regulating the percentage of water in the lime.]

*Damp air* of  $80^\circ C$ . deprives the bleaching-powder of much oxygen, but not of chlorine, much chloride and chlorate being formed. *Dry air* deprives it equally of oxygen, but at the same time splits off some chlorine. *Carbonic acid* in the dry state has little or no action; in the damp state it expels at  $70^\circ$  most of the chlorine (29.58 per cent. of the 34 per cent. contained in the sample), without, of course, acting on calcium chloride. Hence no real  $CaCl_2$  can be assumed to exist in bleaching-powder, and Odling's formula  $Cl-Ca-OCl$  is to be assumed as correct. The *water* in chlorine can be mostly expelled already at  $150^\circ$ ; a few per cent. only at a red heat. The strongest bleaching-powder made in the laboratory contained about 17 per cent., weaker commercial bleaching-powder  $20\frac{1}{2}$  per cent. water.

The analysis of a very good sample of laboratory-made bleaching-powder showed :—

39·89	per cent.	CaO.
43·13	„	available chlorine.
0·29	„	chlorine as chloride (corr. to 0·07 oxygen).
17·00	„	H <sub>2</sub> O (directly estimated).
0·42	„	CO <sub>2</sub> .

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100·73 per cent., of which 0·07 has to be deducted for oxygen.

From this the following composition can be deduced :—

2 CaOCl <sub>2</sub> , H <sub>2</sub> O	82·65
CaCO <sub>3</sub>	0·95
CaCl <sub>2</sub>	0·44
Ca(OH) <sub>2</sub>	6·80
H <sub>2</sub> O	9·16

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100·00

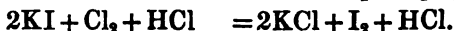
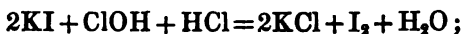
This small quantity of calcium hydrate is not sufficient for the construction of any formula, and must be explained by the assumption, plausible in every respect, that the bleaching-compound mechanically surrounds a portion of the lime and does not allow the chlorine to penetrate to it.

Experiments on the most suitable *temperature* for the formation of bleaching-powder showed that even at 0° bleach of 20 per cent. was obtained. With dry chlorine not much difference was found between 10° and 60°; even at 60° C. we obtained bleach with 40·5 per cent. available chlorine with dry chlorine, or 39·5 per cent. with damp chlorine; but above 60° the percentage rapidly decreased. The strongest bleach (42·5 per cent. with dry, 41 per cent. with damp chlorine) was obtained between 40° and 45° C.; the percentage of the bleach made at that temperature after two months' keeping had only decreased to 39 per cent., which is quite normal.

The *residue* remaining on dissolving the bleaching-powder was found to consist almost entirely of Ca(OH)<sub>2</sub>; but it was not possible to remove the last trace of bleaching chlorine by washing. In the case of very good (43 per cent.) laboratory-made bleaching-powder, the calcium hydrate diminished to 6·2 per cent.

Many experiments were made on the behaviour of bleaching-

powder solutions towards *acids*. As it was frequently necessary to estimate hypochlorous acid along with free chlorine, and as the methods employed by our predecessors were very imperfect, I worked out a very simple method, based on the following reactions:—



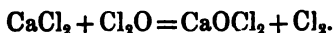
That is to say: on adding potassium iodide and standard hydrochloric acid, in the case of hypochlorous acid each mol. HOCl causes the neutralization of a mol. HCl, but in the case of free chlorine no HCl is neutralized. The free iodine separated is titrated with decinormal thiosulphate, and then the acidity is titrated in the ordinary way. Since HOCl consumes twice as much decinormal thiosulphate as decinormal hydrochloric acid, any excess of the latter over this proportion indicates a corresponding quantity of free chlorine present. With the assistance of this method the behaviour of strong mineral acids and carbonic acid towards solutions of bleaching-powder was investigated (comp. above, the action of  $\text{CO}_2$  on *dry* bleaching-powder). We found that even the strong acids, unless an excess of these was present, *primarily* formed only HOCl; this, of course, also holds good of  $\text{CO}_2$ . Freshly precipitated calcium carbonate was only partially decomposed by free HOCl; part of the latter distils over unchanged. On boiling, the solution of HOCl yields very inconsiderable quantities of oxygen.

Kraut (Ann. Chem. ccxiv. p. 354) objected to Odling's formula that lithia, which is monovalent and therefore not reducible to a formula similar to Odling's, behaves towards chlorine precisely like lime: at  $0^\circ$  it is not acted upon; in the presence of a little water the quantity of chlorine absorbed does not correspond to the total lithia present, but only to two-thirds of it; the bleaching compound always necessarily contains one-third of the base in excess, and is decomposed by  $\text{CO}_2$  just like bleaching-powder. The latter must be represented as containing a mixture of calcium hypochlorite and chloride, which is formed by the action of  $4\text{Cl}$  on  $3\text{Ca}(\text{OH})_2$ , and which is decomposed by  $\text{CO}_2$  in such manner that hypochlorous acid is liberated from the hypochlorite, and that the hypochlorous acid decomposes the calcium chloride by a common reaction with  $\text{CO}_2$ , thus:





Kraut's assertions, which were based on a very few experiments of two of his students, were refuted on all points by an extensive investigation, made by Lunge and Naef (Ann. Chem. ccxix. p. 129; an abstract in Berl. Ber. 1883, p. 840). We showed that Kraut's alleged "common reaction" of  $\text{Cl}_2\text{O}$  and  $\text{CO}_2$  is nothing but a mixing up of two successive phenomena. Hypochlorous acid acts on pure  $\text{CaCl}_2$  with formation of bleaching-powder, distinguished from the ordinary product by not containing an excess of lime, but of calcium chloride, the reaction being:



From bleaching-powder  $\text{CO}_2$  expels only that quantity of chlorine which must be expected from the theory:



The analysis of the gases never showed more than a trace of  $\text{Cl}_2\text{O}$  along with the chlorine, whereas according to Kraut's theory considerable quantities of  $\text{Cl}_2\text{O}$  should have been found. The experiments with lithia made by Kraut's students are altogether wrong, and so are his calculations founded thereon. It is possible to convert not merely 66 per cent. but 88 per cent. of the lithia by chlorine into a bleaching compound, which behaves, however, altogether differently from chloride of lime: at the ordinary temperature it is hardly at all acted upon by  $\text{CO}_2$ , and the gas liberated contains pretty much  $\text{Cl}_2\text{O}$ , together with chlorine. On the other hand, the bivalent metals barium and strontium yield products altogether analogous to chloride of lime in the above respect. This fact affords further support to the view that bleaching-powder (chloride of lime) contains a *compound*  $\text{Cl}-\text{Ca}-\text{OCl}$ , but "chloride of lithia" a *mixture* of  $\text{LiOCl}$  and  $\text{LiCl}$ : of course in the case of a monovalent metal a compound similar to the above cannot possibly be formed.

This investigation was opposed by Kraut (Ann. Chem. ccxxi. p. 108) in extremely violent terms, but without adducing a single new fact. His assertions were again completely refuted by a paper of mine (*ead. loco*, ccxxiii. p. 106).

A paper by Dreyfus (Bull. Soc. Chim. xli. p. 600), who pronounces for Stahl Schmidt's formula, but whose work is full of the grossest errors, has been entirely demolished by Lunge and Schoch (Berl. Ber. 1887, p. 1474).

Mijers (Rec. trav. chim. Pays-Bas, xi. p. 76) gives to bleaching-

powder the formula  $\text{Cl}_2\text{Ca}(\text{OH})_2$ , which he believes to be an important new discovery, but which means nothing but a hydrate of Odling's formula. He also attacks some of my assertions, founded on observed facts, but without the shadow of a proof. I have shown the utter worthlessness of his paper in *Zschr. f. anorg. Chem.* ii. p. 311. A very weak attempt of Mijers to uphold his position (*ibid.* iii. p. 186), which was in reality a complete retreat, has been refuted by me (*ibid.* iii. p. 352).

Sometimes (first by Persoz) the assertion has been made that the *insoluble residue* of bleaching-powder contains a special bleaching compound which acts more distinctively on vegetable fibre than a solution of bleaching-powder. I have induced Mr. Fred. Hodges to examine this subject, with the result that there is no such insoluble compound, or that at all events it is dissolved by prolonged washing, and this solution behaves exactly like ordinary bleaching-powder solution. The alleged distinctive action of the residue could not be established: it must be assumed that the observed damage is caused by fine particles of bleaching-powder settling on the fibre and locally forming concentrated solutions by which cellulose is converted into oxycellulose.

Hutchinson (Engl. patent 13504, 1890) makes the very impracticable proposal to employ the insoluble residue for the preparation of caustic soda from sodium carbonate; the residue formed by this operation is to be separated by a filter-press and to be used over again.

An extensive investigation respecting *the action of metallic oxides on the hypochlorites of the alkalies and of lime* has been made by Blattner (*Bull. Soc. Chim. du Nord*, 1892, p. 58). The precipitated metallic oxides were left in contact with the agents at ordinary temperatures during 15 or 20 days and were daily titrated. The oxides of cobalt, nickel, and copper after three days reduce the total available chlorine of bleaching-powder to chloride. Ferric oxide acts much more slowly, the oxides of manganese and lead very slightly indeed; zinc oxide has no action at all. The concentration of the solution of chloride of lime is not material. The same reactions were exhibited by the metallic oxides in the same order towards hypochlorite of soda (*Eau de Javel*). In this case the strength of the solutions was varied, not merely with respect to their available chlorine, but also to their excess of alkali. Contrary to the common opinion, it turned out that the stability of *Eau de Javel*

does not increase with its alkalinity: this has only a slight, and sometimes the contrary influence. Only the concentration is of importance. Liquors containing 40° Gay-Lussac (12·7 per cent. available chlorine) or less lose part of their available chlorine from day to day in the same ratio; those testing above 40° G.L. lose twice as much, especially during the first few days; here also the decomposition goes on in proportion to the percentage of available chlorine. Dry metallic oxides act much more slowly than in the state of a freshly precipitated paste. The metals themselves act quite similarly to their oxides. This is important for technical purposes, for it shows that copper is least adapted for being brought into contact with bleach liquors; iron comes at a great distance, but is still decidedly injurious; whereas lead has hardly any, and zinc absolutely no injurious action.

Blattner's results as to the part played by cupric oxide towards bleaching-powder solutions may possibly explain the phenomenon, noticed by Gerland (Journ. Soc. Chem. Ind. 1891, p. 25), that bleach liquor obtained by the Deacon process was quickly decomposed when over 40° C., but liquor from the Weldon process only when a copper vessel was employed (Deacon bleach always contains a trace of copper, comp. p. 412).

### *Analysis of Bleaching-Powder and Bleach-Liquors.*

The *technical analysis* of bleaching-powder is exclusively confined to the estimation of its percentage of available chlorine (*chlorometry*). A large number of plans have been proposed for this, the most important of which will now be explained.

The first rational chlorometrical method was introduced, in 1835, by Gay-Lussac (Ann. Chim. Phys. [2] lx. p. 225), and is still the basis of commercial transactions in France. He availed himself of the fact that free chlorine in an acid solution oxidizes arsenious to arsenic acid:



198 parts by weight of arsenious acid are converted into arsenic acid by 142 parts of chlorine; or 1 litre of chlorine, measured at 0° C. and 760 millim. mercurial pressure, weighing 3·17344 grams, oxidizes 4·425 grams  $\text{As}_2\text{O}_3$ . Consequently this quantity of arsenious acid is also oxidized by a certain volume of a liquid

containing exactly 1 litre of chlorine. A standard solution is made by digesting 4.425 grams of pure arsenious acid with hydrochloric acid and 900 cubic centims. of water till completely dissolved, and, after cooling, diluting the solution to exactly 1 litre. Of the bleaching-powder 10 grams are weighed, triturated in a porcelain mortar with a little water to a soft mud, gradually rinsed into a litre bottle, and diluted to 1000 cub. centims. Now 10 cub. centims. of the arsenic solution are taken out with a pipette, coloured blue with a few drops of a solution of indigo in sulphuric acid, and the bleach-solution run in from a burette till the blue colour has just vanished. So long as any arsenious acid is present, the chlorine is taken up by it; so that the indigo is not bleached until all the arsenic has been oxidized. The volume of bleach-solution consumed corresponds to the 10 cub. centims. of chlorine required for oxidizing the 10 cub. centims. of arsenic-solution employed; and the number of cub. centims. of bleach-solution consumed, divided by 1000, gives the number of litres of chlorine gas which can be liberated by 1 kilogram of the bleach. This number is known as Gay-Lussac's degrees; it is the only one used in France, and is also pretty frequently used in continental countries; but Gay-Lussac's analytical method has been abandoned everywhere out of France. The latter is faulty, as with different degrees of dilution and different quantities of acid in excess very varying results are obtained; since chlorine and arsenious acid may coexist in dilute solutions, the bleaching of the indigo is no certain test for the oxidation of all the arsenic; and as, further, the indigo is always partially destroyed at the point where the bleach-solution runs in, the colour becomes fainter and fainter, and the end of the operation is very indistinct (Mohr).

In spite of its imperfections, and although Penot's method, so much superior to it, has also been invented in France, Gay-Lussac's method seems to be still predominant in that country; at least it is the only one described in the last editions of authoritative text-books, such as Payen's '*Précis de Chimie industrielle*' and Frémy's '*Encyclopédie chimique*' (article "*Chlore*," by Kolb).

The designation of the strength of bleaching compounds by Gay-Lussac's degrees, although it is much less rational than that by percentage of bleaching (available) chlorine by weight, is not merely universal in France, but is also general in Italy, Spain, &c.,

and frequently used even in Germany. In England and America the percentage by weight is exclusively used.

The testing method, formerly generally employed in England Germany, and some other countries, was introduced by Graham and improved by Otto. It is founded on the fact that ferrous salts are directly oxidized into ferric salts by bleaching-powder, and that it is easy to discover when no more ferrous salt is present. The reaction is

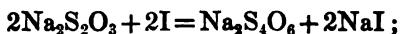


For this purpose ferrous sulphate is usually employed. It is best prepared, according to Otto, in the shape of a fine powder precipitated by alcohol, which is much more slowly oxidized in the air than the ordinary crystals of copperas; but it appears then to contain less than 7 molecules of water, and consequently yields misleading results. Mohr very strongly recommended ammonio-ferrous sulphate; but this ought not to be employed, since Biltz has shown (Wagner's *Jahresb.* 1871, p. 255; 1874, p. 361) that a portion of the chlorine is consumed in decomposing the ammonia. The corresponding sodium compound  $\text{FeNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  is said to be preferable. The molecular weight of  $2(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})$  is 556, and answers to  $2\text{Cl}=71$ ; hence 0.5 gram Cl oxidizes 3.9 ferrous sulphate. This quantity is weighed off, dissolved in about 50 cub. centims. of water, and acidulated with sulphuric acid. Further, exactly 5 grams of the bleaching-powder to be tested are weighed off, most carefully triturated with water to a thin paste, and rinsed into a measuring-tube divided into 100 equal parts, *e.g.*  $\frac{1}{2}$  cub. centim. each. The burette is filled up to the mark with the rinsings and its contents well mixed up. This bleach-solution (which ought to have the appearance of milk and not show any small lumps) is poured with constant agitation into the iron-solution prepared before; and from time to time the mixture is tested for unoxidized iron by taking out a drop with a glass rod and putting it beside one of a solution of potassium ferricyanide quite free from ferrocyanide. When no more blue precipitate, but only a brown coloration ensues, the operation is finished. Thus just as much bleach has been consumed as corresponds to 0.5 gram of chlorine; hence the percentage of available chlorine in the bleach is found by dividing  $100 \times 10 = 1000$  by the number of measures of bleach-solution (made from 5 grams) consumed. Thus, if 29.5 measures

have been consumed, the bleach holds  $\frac{1000}{29.5} = 33.5$  per cent. of available chlorine.

Graham and Otto's process cannot be recommended at all. It requires exact weighings of bleaching-powder and iron salt for every single test. It is not easy to make from 5 grams of bleach, with all rinsings, a measure of 50 cub. centims. really free from small lumps; the burette must be often shaken to keep the liquid in the same state. When the proper point has been exceeded, correction is impossible, and a new test must be made. Lastly, the accuracy of the test entirely depends upon the absolute purity of the iron-salt employed, unless the very tedious plan is adopted of dissolving pure iron wire for each test. Hence the process is much more troublesome and tedious even in manipulation, and requires more practice, than the iodine method or Penot's arsenic method. And, after all, it is decidedly inaccurate; for with the best stirring it is impossible to prevent an escape of chlorine when the bleach-solution is being poured into the acid liquid: the results obtained are always too low, and that by 1 or 2 per cent. Another source of error is, that any chlorate present acts, even when cold, upon ferrous sulphate in an acid solution, as was shown by Wright (*Chem. News*, xvi. p. 171); the same perhaps holds good of Wagner's test, in which also an acid solution is employed, whilst Penot's test, in an alkaline solution, is not at all influenced by the presence of chlorates.

Another, much more trustworthy method is the iodine method, indicated by Bunsen and improved by Wagner, who substituted for the solution of sulphurous acid one of sodium thiosulphate. It utilizes the fact that bleaching-powder liberates from a potassium-iodide solution in the presence of free hydrochloric acid a quantity of iodine equivalent to the available chlorine, the iodine remaining dissolved in the excess of potassium iodide. On addition of sodium thiosulphate, tetrathionate is formed, according to the equation



so that, after the iodine has been completely used up, the liquid, previously dark brown or coloured blue by starch, is decolorized. 10 grams of bleaching-powder are ground up with water, diluted to one litre; 100 cub. centims. (= 1 gram of bleach) are taken out, and to these are added 25 cub. centims. of a 10-per-cent. solution

of potassium iodide and hydrochloric acid till the reaction is acid. To this brown liquid the operator adds decinormal thiosulphate solution (containing 24.8 grams of that salt per litre) from a burette, at the same time stirring. The brown liquid gradually turns lighter, and at last becomes colourless, completing the operation. The transition is quite sharp and unmistakable. The number of cub. centims. of thiosulphate consumed, multiplied by 0.355, shows the percentage of available chlorine in the bleaching-powder. (Some precautions to be used in testing with thiosulphate have been mentioned above, p. 124.) Wagner's process is very convenient and quickly executed; and in the absence of chlorate it is also very exact; but in the presence of that salt it is inaccurate, unless the slightest excess of HCl be avoided, which is a very difficult matter. Chlorate acts equally upon KI in the presence of HCl; but its chlorine is useless to the consumer. This assertion (made by Mohr) is denied by Wagner himself, and has also been disproved by Winkler (*Dingl. Journ.* cxviii. p. 143). The process is also somewhat expensive as an every-day test, on account of the potassium iodide. Wagner's proposal to employ the decolorized solutions over again for dissolving iodine is not feasible, on account of the dilution; and Mohr asserts that it is inaccurate in the presence of alkaline carbonates.

The process which has recently been employed in most laboratories (elsewhere than in France) is titration with an alkaline arsenite-solution (while Gay-Lussac had employed an acid solution). This process, introduced by Penot, fully deserves the preference given to it, on account of its being entirely free from sources of error, and its great simplicity and facility of execution. The reaction is the same as in Gay-Lussac's process; but by employing an alkaline liquid any escape of chlorine is avoided; and the indicator, iodized starch-paper, has none of the drawbacks attaching to the indigo-solution.

A standard solution is made by dissolving  $\frac{1}{10}$  molecule = 4.95 grams of pure powdered arsenious acid in four times its weight of pure sodium carbonate or bicarbonate and about 200 grams of boiling water. Neither the arsenic nor the soda must contain any oxidizable sulphur compounds; otherwise the solution will not keep. Hence it is safest to employ sodium bicarbonate, which is always pure in this respect, and to test the arsenious acid (of which the porcelain-like pieces occurring in commerce are usually

quite pure) by incipient sublimation between two watch-glasses; the red arsenic sulphide, subliming first, is easily recognized. A small sample, heated on platinum foil, should be completely volatilized. The arsenious acid has the convenient property of not being hygroscopic, and hence is easily weighed with accuracy. When it has been completely dissolved, the liquid is diluted to a litre; it keeps wholly unchanged for years, even in bottles not quite full. The test-paper is made by boiling starch for some time with one hundred times its weight of water, filtering, adding a little pure potassium iodide, and soaking Swedish filtering-paper in the liquid.

For carrying out the operation, a bleaching-powder solution is made just as described above, viz. by grinding the powder with a little water in a small mortar with its spout greased, diluting with more water, rinsing out, &c. Sometimes warm water is used; but this should be done cautiously, as such solutions of bleach quickly spoil. I weigh each time 7·100 grams of bleach, which is made up to a litre; for each operation 50 cub. centims. (= 0·355 gram) are taken. This, if it contained 100 per cent. Cl, would require 100 cub. centims. of the  $\frac{1}{10}$  molecular arsenic-solution; hence the number of cub. centims. of the arsenic-solution actually used shows without any calculation how much per cent. of available chlorine is present in the bleaching-powder. The testing is performed thus:—The 50 cub. centims. of bleach-solution are pipetted into a beaker, which is agitated while not quite so much arsenic-solution as is thought necessary is poured in from a pinchcock burette; a drop of the mixture is put on the potassium-iodide starch-paper. According to the depth of colour (which with a very large excess of chlorine is not blue, but brown), more or less arsenic is poured in again, and again tested, till at last no spot is produced on the test-paper. With a little practice, only four or five testings need be made in order to titrate down to  $\frac{1}{10}$  or even  $\frac{1}{20}$  per cent.

Mohr adds at once an excess of arsenic-solution, then a little starch-solution, and titrates back with a solution of iodine equivalent to the arsenic-solution (containing 12·70 grams of iodine and about 25 grams of KI per litre). Thus the testing of spots is saved; but two standard liquids are required instead of one, and the iodine-liquid cannot be employed even in a pinchcock burette.



Hence Penot's original process is more usually employed in factories.

No mention will here be made of the great number of other chlorometric methods, none of which has any advantage over Penot's, and nearly all of which are inferior to it in some respect. Only the gas-volumetric method, employing hydrogen peroxide, will be described, as it is an excellent check for Penot's method.

This method is described in *Journ. Soc. Chem. Ind.* 1890, p. 22; it is carried out in a nitrometer or gas-volumeter, with a reaction-flask attached to it, just as in testing manganese ore by this method (p. 278). The solution of bleaching-powder is run by means of a pipette into the outer space of the flask, the hydrogen peroxide into the central tube; the operation is performed just as with manganese ore, and the reading is taken at once. The reaction being  $\text{CaOCl}_2 + \text{H}_2\text{O}_2 = \text{CaCl}_2 + \text{H}_2\text{O} + \text{O}_2$ , the volume of oxygen given off equals that of the bleaching-chlorine. If 20 grams bleaching-powder is dissolved up to 500 cub. centims., and 5 cub. centims. (=0.2 gram bleach) is employed for testing, each cub. centim. of oxygen, reduced to 0° and 760 millims., answers to 5 degrees Gay-Lussac, or 1.58 per cent. by weight of available chlorine. If 7.917 grams bleaching-powder is dissolved to 250 cub. centims., and 10 cub. centims. is employed for analysis, each cub. centim. oxygen immediately indicates 1 per cent. of available chlorine. The hydrogen peroxide should be made just perceptibly alkaline (as shown by a slight flocculent precipitate). The results are about 0.2 per cent. higher than with Penot's method.

In all prescriptions for testing bleaching-powder stress is laid upon employing, not a clear, but a turbid, shaken-up solution of bleach for titrating. The reason is because the bleaching chlorine is never all dissolved, but a portion of it remains in the sediment, and hence less is always found on titrating the clear solution than with the turbid liquid. But undoubtedly this custom is not altogether justifiable; for the consumers must nearly always use for their purposes, not the turbid liquid, but only a clear solution. This would not matter very much if the proportion of available chlorine in the liquid to that in the sediment were always the same; but while there are no experiments extant upon this point such

constancy of proportion is not likely to exist, since on dissolving some descriptions of bleach they behave very differently from others, according to the nature of the lime. A general agreement to titrate only the clear solution, and to abate accordingly the requirement of 35 per cent., would be much more rational.

The following table (calculated by Pattinson, Chem. News, xix. p. 111) shows the proportion between the Gay-Lussac degrees, used in France, and the percentage of available chlorine as designated in England, Germany, &c., on the assumption of 35·46 for the molecular weight of chlorine, 0·08961 gram for the weight of 1 litre of hydrogen at 0° and 760 millims. pressure, and, correspondingly, 3·17763 grams for 1 litre of chlorine gas.

French degrees.	Per cent. Chlorine.	French degrees.	Per cent. Chlorine.	French degrees.	Per cent. Chlorine.
63 .....	20·02	85 .....	27·01	107 .....	34·00
64 .....	20·34	86 .....	27·33	108 .....	34·32
65 .....	20·65	87 .....	27·65	109 .....	34·64
66 .....	20·97	88 .....	27·96	110 .....	34·95
67 .....	21·29	89 .....	28·28	111 .....	35·27
68 .....	21·61	90 .....	28·60	112 .....	35·59
69 .....	21·93	91 .....	28·92	113 .....	35·91
70 .....	22·24	92 .....	29·23	114 .....	36·22
71 .....	22·56	93 .....	29·55	115 .....	36·54
72 .....	22·88	94 .....	29·87	116 .....	36·86
73 .....	23·20	95 .....	30·19	117 .....	37·18
74 .....	23·51	96 .....	30·51	118 .....	37·50
75 .....	23·83	97 .....	30·82	119 .....	37·81
76 .....	24·15	98 .....	31·14	120 .....	38·13
77 .....	24·47	99 .....	31·46	121 .....	38·45
78 .....	24·79	100 .....	31·78	122 .....	38·77
79 .....	25·10	101 .....	32·09	123 .....	39·08
80 .....	25·42	102 .....	32·41	124 .....	39·40
81 .....	25·74	103 .....	32·73	125 .....	39·72
82 .....	26·06	104 .....	33·05	126 .....	40·04
83 .....	26·37	105 .....	33·36	127 .....	40·36
84 .....	26·69	106 .....	33·68	128 .....	40·67

In testing bleaching-powder a proper kind of *sampling* is very important. The result may vary by several per cent., according to whether more or less care has been taken in that respect. At all events the sampling must be performed in a dry place, protected against wind if practicable, and as quickly as possible. When working in a warehouse, or still more easily at the works themselves before the last cooping up of the casks, it is a

good plan to open the upper end of the cask, to put one's arm as deeply as possible into the cask, take out a handful of bleach and throw it into a large, wide-mouthed bottle, which thus receives samples from every cask collected, and in which they are at last intimately mixed. Where this kind of sampling is not feasible, the casks must be bored with an auger, and the samples thus obtained are also thrown into the above-mentioned wide-mouthed bottle, which is instantly corked each time. A suitable auger is shown Vol. II. p. 99. Superior to this is Angerstein's sampler, Germ. pat. No. 26680, consisting of a long tube, half open in the lower half and provided with a point at the lower end. This admits of taking a sample from the middle of the cask without an admixture of the upper layers.

The bleaching-powder samples must be at once divided among a suitable number of small bottles, which are well corked and sealed; they must be kept in a cool and *dark* place, and must be employed for testing without unnecessary delay.

For many purposes the following *table of the specific gravities of bleaching-powder solutions*, published by me in *Zsch. f. angew. Ch.* 1893, p. 326, will be useful. It was made with a liquor prepared from good commercial bleaching-powder and composed as follows:—

Available chlorine .....	72·17	grams	per	litre.
Chlorine as chloride .....	6·74	”	”	”
Chlorine as chlorate .....	0·13	”	”	”
Lime.....	65·53	”	”	”

corresponding to:

$\text{CaOCl}_2$ .....	129·09	grams	per	litre.
$\text{CaCl}_2$ .....	10·54	”	”	”
$\text{CaCl}_2\text{O}_6$ .....	0·38	”	”	”
$\text{CaO}_2\text{H}_2$ .....	4·21	”	”	”

This analysis does not constitute an ideal bleaching-powder fresh from the works, but a good commercial article, as found in trade, and is therefore more practically useful. It is, of course, not applicable to old stuff, containing much excess of calcium chloride and chlorate.

Spec. grav. at 15° C.	Avail. chlorine grams per litre.	Spec. grav. at 15° C.	Avail. chlorine grams per litre.
1·1155	71·79	1·0600	35·81
1·1150	71·50	1·0550	32·68
1·1105	68·40	1·0500	29·60
1·1100	68·00	1·0450	26·62
1·1060	65·33	1·0400	23·75
1·1050	64·50	1·0350	20·44
1·1000	61·50	1·0300	17·36
1·0950	58·40	1·0250	14·47
1·0900	55·18	1·0200	11·41
1·0850	52·27	1·0150	8·41
1·0800	49·96	1·0100	5·58
1·0750	45·70	1·0050	2·71
1·0700	42·31	1·0025	1·40
1·0650	39·10	1·0000	trace.

The decrease of available chlorine on keeping solutions has been examined by Lunge and Landolt (Chem. Ind. 1885, p. 343). When kept out of contact with air and in the dark, the titre of the solution had not perceptibly decreased after 24 days, and very slightly so after 33 days. When kept open in the dark it lost nothing up to 12 days, and about  $\frac{1}{3}$  of its strength after 33 days. But *light* has a powerful action. The titre of a solution kept in a stoppered bottle in diffused daylight decreased from day to day, and after 33 days did not amount to much over one-fourth of the original strength. Observations on the stability of *solid* bleaching-powder are given in the next chapter.

#### *Complete Analysis of Bleaching-Chlorine Compounds.*

This embraces estimations of the available chlorine, the chlorine present as chloride and chlorate, the carbonic acid and the bases.

The most convenient method for estimating the *chloride* is that which I have indicated (p. 399). The liquid remaining from Penot's method, in which the available chlorine has been reduced to chloride, is acidulated with nitric acid, and the chlorides are gravimetrically estimated by silver nitrate; or else, without acidulating, volumetrically, in which case the silver arseniate acts in the same way as the silver chromate prescribed by Mohr, but with much greater delicacy. On subtracting the available chlorine from the total chloride, we find the quantity of the original chloride.

*Chlorate* is found by estimating together the available chlorine and the chlorate by the ferrous sulphate method described in Chapter XXII., and subtracting the former from the sum.

*Lime* is usually estimated by boiling the sample with HCl and precipitating the filtrate with  $\text{NH}_3$  and ammonium oxalate.

For estimating *free and carbonated alkali* in Eau de Javel, Blattner (Bull. Soc. Chim. du Nord, 1891, i. p. 116) has given the following method:—Phenolphthalein retains its pink colour in a solution of hypochlorites so long as any caustic soda is present, but when the caustic soda is exhausted its colour is destroyed by free chlorine, and is not restored by adding alkali: 10 c. c. of the Eau de Javel is put in a 250 c. c. flask, 150 c. c. of boiled and cooled distilled water and a few drops of a 1 per cent. alcoholic phenolphthalein solution are added, and standard hydrochloric or sulphuric acid is run in. If, after adding a fresh drop of phenolphthalein, the colour is removed by 5 seconds' shaking, the titration is finished, and each c. c. of standard acid employed shows 0.031 gram  $\text{Na}_2\text{O}$  or 0.040 gram NaOH present as caustic soda. *Total alkali*, i. e. carbonate and caustic, is found in another sample by boiling with ammonia to decompose the hypochlorite, expelling all ammonia by further boiling, and titrating with standard acid.

## CHAPTER XX.

## THE MANUFACTURE OF BLEACHING-POWDER.

## LIME.

THE lime intended for manufacturing bleach must be of special purity; on this depends to a great extent the possibility of making strong and durable bleaching-powder. This means, first, that the limestone should be sufficiently pure, and that it should be burnt as well as possible. Most manufacturers, in order to make sure of the last point, prefer burning the lime for themselves. The Lancashire manufacturers enjoy the advantage of getting, delivered by rail to their works, an extremely pure and well-burnt limestone from Buxton, which has the agreeable property that, on slaking it, all the unburnt portions remain behind as stony pieces (yelks), so that the fine powder of calcium hydrate is almost completely free from carbonate. Most descriptions of lime do not behave in this way; and the bleach-manufacturers can ensure their sufficient freedom from carbonic acid only by taking the burning in hand themselves.

Limestone, to be employed for bleach, must contain very few constituents insoluble in acid (clay, sand, &c.), because otherwise (as of course they would not be converted into bleach) the strongest article could not be made. Moreover bleach containing clay settles imperfectly and very slowly on being dissolved, and is on this account disliked by bleachers, paper-makers, &c. Consumers also require a white article, which excludes iron, manganese, &c. These metals are even said to impair the durability of bleach; but this is not certain. Magnesia is also very much disliked, because, it is said, the deliquescence of magnesium chloride interferes with the stability of bleach. This does not appear to have been certainly proved; but, for instance, the magnesian limestones found on the

Tyne, from the Coal-measures and the Permian, have been found quite unsuitable for bleach-making. On the other hand, a dark colour of the limestone, caused by bituminous matters, is quite harmless, as these are destroyed by the burning. Balard (*Rapport du Jury*, vii. p. 49) asserts that the physical are even more important than the chemical properties of limestone in regard to its suitability for bleach-making; according to him, pure but crystalline limestone is not suitable, while another description, containing more than 2 per cent. sand and clay, is preferred at Chauny. This assertion is contradicted by experience. I have never made finer and stronger (39 to 40 per cent.) bleach than with a cargo of distinctly crystalline limestone from the north of Ireland which I got by chance. At Chauny (cited by Balard), at any rate at that time, as a rule the bleach made contained not 35, but only 80 to 32 per cent.

It cannot, however, be denied that the physical properties of the limestone, or rather of the lime made from it, have a good deal to do with the quality of the bleach. "Fat" lime, which slakes quickly and yields a fine, light powder, absorbs chlorine much more quickly than poor lime which on slaking yields a gritty powder, even when analysis does not show any difference between them. Bleach from fat lime also keeps much better than that from poor lime. The latter contains much more chlorate, and is more ready to decompose with evolution of gas, but the former more easily attracts moisture from the air and becomes pasty (Wright, *Chem. News*, xvi. p. 126).

On the Tyne the usual material for bleach-making is a hard chalk closely resembling limestone, from the lower reaches of the Seine, whence it is brought by colliers as ballast, and is known as "French cliff." It is very pure calcium carbonate, contains next to no iron, and only fractions of 1 per cent. of constituents insoluble in hydrochloric acid. It is also tested by scraping with a knife, when it should yield a floury, not a gritty powder. The bleach made from it is much more bulky than that from Buxton or Irish limestone; so that about  $\frac{1}{3}$  more casks are required for it. The solutions of bleach made from cliff do not settle so quickly as those of limestone bleach; bleachers usually prefer the latter, paper-makers the former.

The *burning* of the limestone may take place in any lime-kiln, so long as the lime cannot be contaminated by the ashes of the fuel,

or as the more impure portions are kept out and used for mortar &c. The most rational are the circular or other continuous furnaces, which are now also in use at Buxton. But a bleach manufacturer cannot possibly manage with furnaces turning out such

Fig. 139.

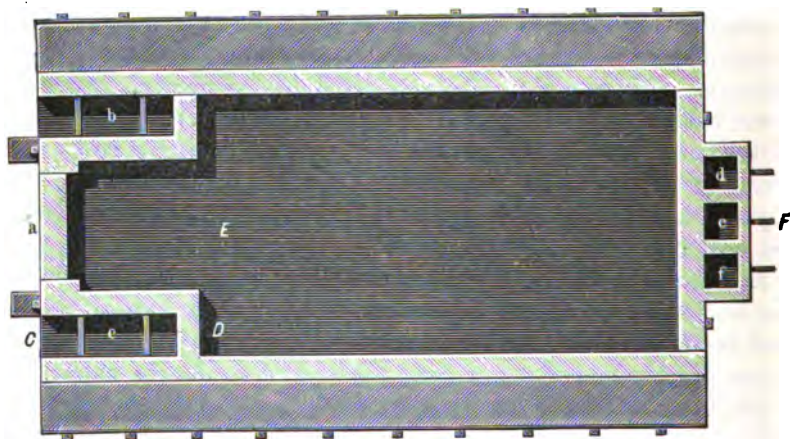
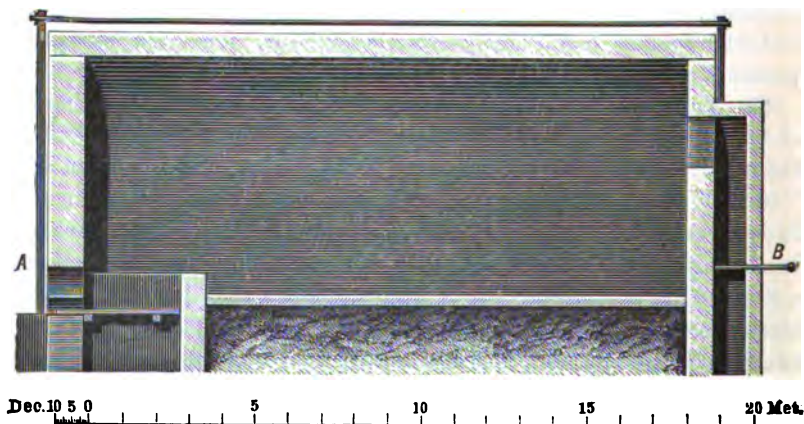


Fig. 140.



large quantities; he must therefore build kilns of another kind. Those employed on the Tyne are of the shape of a horizontal rever-



beratory furnace, as shown in figs. 139–142. Fig. 139 is a plan on the line AB of the sectional elevation, fig. 140; the latter is taken on the line C D E F of the plan. Fig. 141 is a front elevation, fig. 142 a back elevation. In front there is a large overarched

Fig. 141.

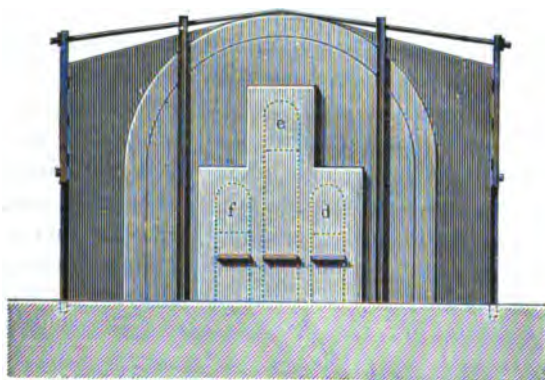
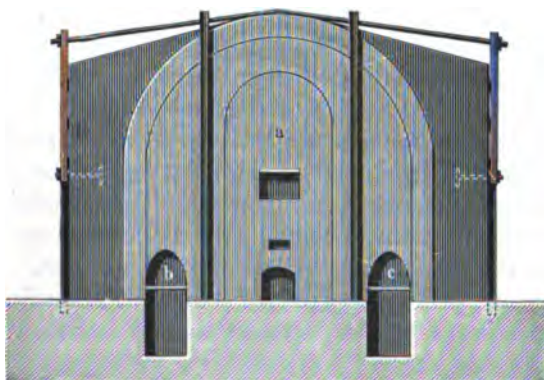


Fig. 142.



opening, *a*, for charging and discharging the kiln; after putting in the limestone, it is closed by a temporary wall, in which the three stoke- and peep-holes seen in fig. 142 are left. Besides, there are the small fireplaces *b* and *c* with grates: sometimes the latter are wanting, and the coals are heaped up behind the stoke-hole; but that is not a good arrangement. In the semicircular arch

which forms the kiln-roof, one or two circular holes, 14 inches wide, are made, but covered up during the burning; they serve for more quickly cooling and airing the kiln. Both the arch and the lining of the kiln all over consist of the best fire-bricks; and the kiln is well braced with uprights and tie-rods. Three snore-holes *d, e, f*, each of them connected with a small shaft and damper, carry away the products of combustion; only below ground the three shafts combine to form a main flue leading to a good chimney. In this way the draught can be regulated equally all over the kiln.

This kiln is intended for bituminous coal. For sandy coal or brown coal a gas-producer is to be preferred for a calcining-furnace, unless the horizontal kiln be replaced by an upright one.

The limestone is put in thus: from the largest lumps (12 to 15 inches wide) three flues are made, corresponding to the stoke-holes and snore-holes; they are covered up with larger blocks, these with smaller lumps, and the smallest (down to the size of a fist) on the top, the kiln being filled right up to the roof. Of course the commencement is made at the back end, and a section of an arm's length finished right up to the roof before the next one is begun. At last the door is walled up as drawn, leaving the draught- and stoke-holes, which are closed with loose iron plates. The firing is now begun from all three stoke-holes, and is continued till the whole contents of the kiln have been burnt to quicklime, but not burnt "dead." This point is reached when a look through the peep-hole shows that the kiln is white-hot up to the roof, and that the charge has sufficiently settled down, owing to the diminution of volume of the limestone in being converted into quicklime. The exact amount of this cannot be stated, as it depends upon the size and shape of the kiln and the nature of the limestone. Although regard for economy of fuel might seem to point to making the kiln very long, this is not feasible, because the bad portions would be burnt too late, and the first portions would consequently be already burnt dead. The dimensions as drawn are proved to be right by experience. The lime is well burnt when it contains less than 2 per cent.  $\text{CO}_2$ ; if the latter exceeds 3 per cent., the lime should be rejected altogether for bleach-making.

A kiln of the size represented holds about 10 tons of limestone, and requires about 5 tons of coals for a burning. With good coals and careful teasing, the burning lasts four days and nights, some-

times five. At the end all the openings are plastered up, also the dampers, lest the kiln should crack by cooling too quickly; after 24 hours the dampers, ash-pits, and top-holes are opened, then also the temporary front wall; and as soon as the kiln has cooled down so that it can be entered, the lime is taken out. If, however, for any reason the lime is not required at once, but is to be kept for some time, the openings are left plastered up as well as possible: the quicklime is then found perfectly good even after months.

Interesting experiments on the temperatures at which, on the one hand,  $\text{CaO}$  absorbs  $\text{CO}_2$ , and, on the other hand,  $\text{CaCO}_3$  is dissociated, have been made by Birnbaum and Mahn (Ber. deut. chem. Ges. xii. p. 1547).

*Slaking* the quicklime is very simple work. The lime is spread on a brick floor (protected from rain) to a thickness of 12 or 15 inches, and water sprinkled over it by a watering-pot or a rose attached to a water-hose, till the formation of calcium hydrate is indicated by the well-known appearance of heating, emission of steam, and swelling-up of the lime. Every portion of the lime must be turned over with a spade, in order to promote its slaking, and a little water added from time to time, till at last every thing that can be slaked at all has fallen to a light fine powder. The workmen protect their mouths and noses during this operation, and during the sifting of the lime and charging of the chambers, by "muzzles" such as will be described hereafter. The large unslaked pieces are picked out and thrown away, if they are pebbles or flints; and any pieces of unburnt limestone or lime burnt dead can be ground and employed in the soda-mixture or for neutralizing the manganese-liquors in the Weldon process; but they may not after grinding be mixed with the sifted calcium hydrate, as stated by some authors.

The calcium hydrate must in any case be *sifted* through brass or iron wire-gauze or hair sieves. At some works sieves with 12 holes, at others sieves with 25 holes to the linear inch are used. It is found that the finer the lime is sifted the better it absorbs the chlorine. The sieves, cylindrical or hexagonal, lying in a closed box in an inclined position, the hydrate is put in at the higher end; and at the other end only the coarse particles are brought out by the sieves, all the fine dust now being found in the box. The coarse parts (lime riddlings) are employed for mortar, &c. At larger works the turning of the sieve is done by a small steam-engine,

which also drives a revolving brush inside it; thus the powder is pressed against the wires, and there is much less waste in the shape of "riddlings."

Mechanical lime-slaking and sifting apparatus have been described by Wackernie and Rousseau (Fischer's Jahresb. 1883, p. 703); Pfeiffer (Engl. pat. 43, 1888); Heyer (Germ. pat. 46728).

The sifted lime is either kept in large wooden boxes or in small casks, arranged for easy carriage to the chambers (old petroleum-casks). It has been found that lime freshly slaked is not so suitable for bleach-making as when it has been lying for a few days. This long-known fact has been sometimes attributed to some mysterious change, or even to the absorption of a little carbonic acid and moisture from the air—which is quite erroneous; such absorption should, on the contrary, be prevented. The true cause is simply that the lime requires some little time to be slaked completely through and to cool down entirely—the latter being a slow process, owing to the loose, porous state of calcium hydrate and its being a bad conductor of heat. If some manufacturers, as is stated, avoid the action of sunshine on the lime, this must be for the same reason, viz. because the heat of the sun retards the cooling.

It is a perfectly established fact that the lime from which bleach is to be made should not be dry  $\text{Ca(OH)}_2$ , but should contain some water in excess, although it has been proved, contrary to previous assertions, that even perfectly dry calcium hydrate absorbs chlorine (comp. p. 424). The former statements concerning the quantity of water required over and above that necessary for the formation of hydrate (23.5 per cent.) were very uncertain. By the investigations made by myself together with Schäppi, it has been ascertained that the best amount of excess of water, when working with absolutely dry chlorine, is 4 per cent.; with damp chlorine, as it is always employed in manufacturing practice, there must be only about 2 per cent. of water over and above the calcium hydrate. The special rules followed at Aussig have been already quoted on p. 424.

A larger proportion of water favours the absorption of chlorine; but then close clumps are formed which enclose much undecomposed lime. There are lumps found even in perfectly good and strong bleach; but these are dry, easily broken, and porous, and changed into bleach right to the core; they cannot be confounded with the damp lumps formed by damp lime and especially by moist chlorine. Under no circumstances should any particles of unslaked lime get into the bleach-chambers.

*The Bleaching-powder Chambers.*

The action of the chlorine (evolved by any sort of process) upon the lime takes place, of course, in very different apparatus, according to whether dry or liquid bleach is to be made—that is, whether calcium hydrate or milk of lime is employed. We shall first treat of the former and much more important kind.

The lime is treated in the so-called bleaching-powder chambers or “boxes,” each of which consists of a closed space built of a material resisting the action of chlorine gas, but which widely differ as to their sizes, their inner arrangements, and the material they are formed of. During the first period the chambers were made of wood, very tightly joined together in double layers, and coated with a thick paint of asphalt. Such wooden chambers cannot be kept tight if the pressure of gas gets beyond a very moderate amount, and hence are useless for strong bleach. Other chambers (now very much more rarely found than formerly) are made of tarred sand-stone flags or slates, the flags being joined together by rabbets and tar and fireclay. These chambers are gas-tight enough, if properly built and standing on a substantial foundation (which prevents settling); but they are unsuited for large works, because they are very costly, and can only be made of a moderate size, which also involves much labour. They can be made larger, if the top is not made of stone flags, but of tarred wood; but this plan again waives the advantage of a substantial erection. In order to better utilize the expensive stone chambers, they are mostly provided with stone shelves (sometimes, but very wrongly, with wooden shelves, from which splinters get into the bleach), so that a larger quantity of lime can be got into them. This kind of erection existed at many English works a number of years ago; but it has been given up almost entirely, since it has been found that even in a chamber 6 feet high the lime at the bottom absorbs the whole of the chlorine; the latter, being much heavier than air, always tends to sink down when the layers below have become poorer in chlorine by absorption. The shelves thus only cause much complication, and especially much labour, as they are only accessible sideways; and they compel the employment of small and consequently expensive chambers. Moreover the contents of chambers with shelves easily become heated, which prevents the turning-out of strong bleach.

Such chambers were formerly built in France in sets of six or eight, each of them consisting of a brick shell of 8 × 8 feet internal

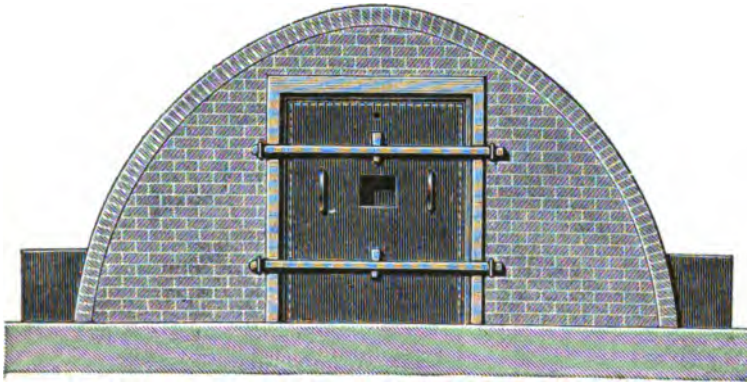
width, and from 8 to 10 feet high, with four or five shelves of stone slabs, 3 inches thick, which by suitable openings at opposite sides caused the chlorine gas to travel in a zigzag manner. The lime (about 6 cwt. for each chamber) was put upon the shelves 4 inches thick, and the chlorine was slowly passed in for 36 to 48 hours, after which the chamber was left standing for another 24 hours, so that each chamber could be furnished twice a week.

At all (or at least nearly all) large works the stone or wood chambers with shelves have been given up long since (apart from the Deacon process), and have been replaced by large chambers, which permit working inside them, and finishing larger quantities of bleach in one operation. Such chambers are always a little above a man's height, say  $6\frac{1}{2}$  feet. It is sometimes stated that they need be only 5 feet high, so that a man may work in them in a bent position: but this would be most reprehensible economy; for the bleach-chamber work, as it is, is so laborious and irksome for the men, that it is out of the question to make it even worse by compelling them to work in a bent position. Even reasons of self-interest, let alone the claims of humanity, forbid this; for the work cannot be properly done in that position. Still less can we approve of making large leaden chambers only 3 feet 3 inches high (as I have myself seen them in one place); for in these the work can only be done from without.

The *area* of the chambers is now much larger than formerly. Chambers are made 33 feet wide and 66, 80, or even 100 feet long—that is, covering as large a ground-space as vitriol-chambers. It is said that large chambers work more regularly than small ones; at any rate they cause less labour and permit a more complete utilization of the chlorine gas. For turning out one ton of bleach per week very different areas are employed at different works. According to a table, given in the 19th Alkali Inspectors' Report, p. 29, the chamber area in the Lancashire district varied between 134 and 398 superficial feet, and averaged 181 superficial feet. But as this embraced some notoriously inadequate cases, the 21st Report (p. 12) recommends a minimum of 200 superficial feet per ton per week (of six days). This suits not merely the case where thicker (4-inch) layers of lime are employed, which necessitates turning over and gassing several times, but also the case where the bleaching-powder is finished by one gassing, by making the layer of lime only 1 or 2 inches thick.

As for the *material*, chambers of a medium size are made of brickwork, larger ones of lead or sometimes of cast-iron. A brick chamber, such as was frequently met with formerly, is shown in front elevation in fig. 143. It is an elliptical arch, of 13 feet span

Fig. 143.



and 6 feet 6 inches high in the centre, only  $4\frac{1}{2}$  inches thick, set with good Portland cement. It can be constructed of good, well-moulded, machine-made common bricks, since the interior of the chambers must in any case be covered with a coating of cement and painted with tar several times. Small abutments, as shown in the figure, add to the stability of the arch, which with good cement is very considerable. The two gable walls are put in last; they must be fitted in very tightly, lest they become detached from the arch by settling down. In each gable-end a stone door-frame is put, provided with a rabbet to receive the door. This is sometimes made of two courses of boards crossing each other, with tarred canvas between, and tarred outside; but such wooden doors, even if well made, do not keep gas-tight very long, unless they are internally coated with sheet lead, which is the usual course taken on the Continent. Another plan is to employ iron doors of  $\frac{1}{4}$ -inch boiler-plate, protected from the action of chlorine by frequently repeated painting with oxide-of-iron paint. The doors are fastened, after plastering the rabbets with lime-putty, each by two horizontal iron bars, the ends of which pass through eyes let into the wall; they are pressed in the centre against the door, and press this against the rabbet. Of course any other way of

fastening the doors may be chosen ; it is usual to hang them on bands. A very convenient plan is also to employ small cranes by means of which one man can easily handle a heavy door. Since in this case their weight is taken off, they may even be made of cast iron. Each door has a hole about 8 inches square to receive a glass pane, on the top a 1-inch hole for letting out the air, and two handles.

The *chamber-floors* are constructed in various ways. Very durable, but very expensive and rarely applied, is a pavement of large stone flags ; brick pavements, even of fire-bricks, very soon become uneven and make the bleach impure. Floors made of deals of various descriptions have been tried frequently, but have always failed ; so have floors of ordinary cement concrete. But the best results have been obtained by asphalt concrete, in applying which the same mixtures and apparatus are employed as in asphaltting public streets. First a bottom of broken bricks or stones of the size of road-metal is made ; upon this the usual mixture of asphalt and sand is cast and perfectly levelled by hot irons. Thus one piece of the floor is finished after the other ; and the butt joints are united by partial melting.

Whilst, for obvious reasons, brick chambers cannot be made much wider than the above-mentioned, no such limit exists for *lead* or *iron* chambers. Chambers made of cast-iron plates, joined by flanges and screw-bolts, were at one time the fashion in Lancashire. A good coat or two of oxide-of-iron paint protects them very well from chlorine ; and it was expected that they would last almost for ever. But they went again out of favour, especially because, in spite of all painting, the bleach is always stained yellow where it comes near the sides. Elsewhere generally lead chambers are employed, made of 5- or 6-lb. lead, similarly to vitriol-chambers, up to 100 feet length and 33 feet width. Such a chamber, cut right through, is shown in fig. 144 in isometrical view.

On a properly levelled place a timber framework of sole-trees and crown-trees, *a*, and tenoned-in uprights, *b*, is made. To this are fastened sheets of lead by turning their upper margin round the crown-tree, nailing them to this and by means of straps to the uprights. At the bottom they reach further down than the floor, and are turned inwards 6 or 12 inches and nailed against the sole-tree. The lead top is hung from joists by means of straps, exactly



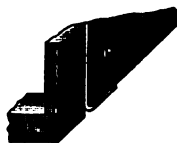
like a vitriol-chamber. In the case of very wide chambers (of 30 feet and upwards), where the top joists would have too great a span, there is a middle row of iron columns placed inside the chamber, carrying a longitudinal girder; all iron and wood is

Fig. 144.



covered with lead. The asphalt bottom is made last, exactly as described above for brick chambers; and in order to keep the joint round the edges tight (which is always facilitated by the lead reaching so far inwards), upright boards, *c*, about 10 inches high, are placed all round the chamber, 2 inches away from the sides, and the space between this and the lead is filled with melted asphalt, forming one mass with the floor itself. This is shown in detail in fig. 145. A more expensive plan, but cheapest in the end, on account of avoiding all repairs, is this: to cover the whole floor with a sheet of lead, which is burned to the sides of the chamber and is covered with stone slabs, which are put in dry but close together, a thin layer of sand having been first put on the lead.

Fig. 145.



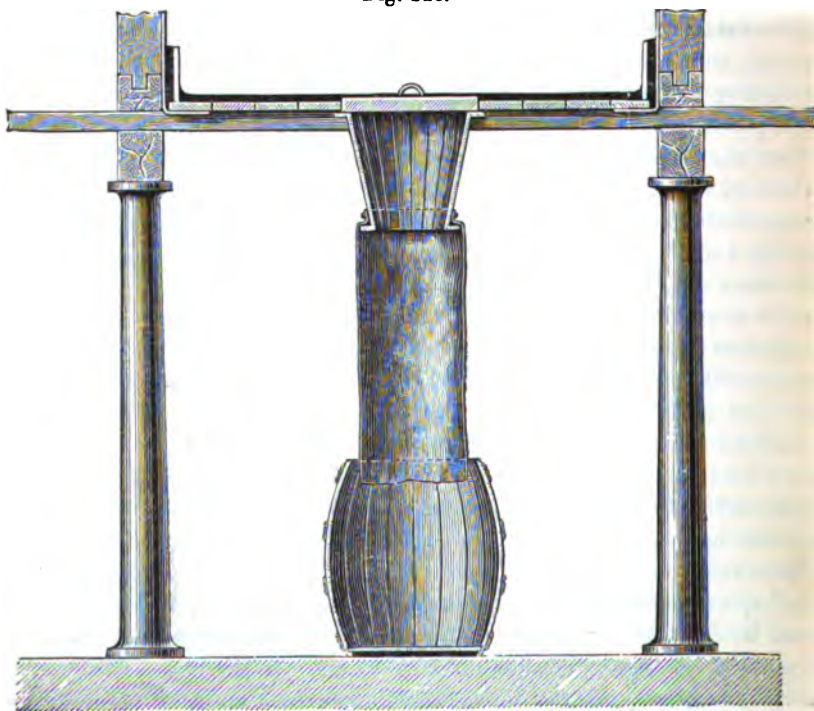
The doors of lead chambers are made of iron, or wood covered with lead, just like those of brick chambers (p. 449). Both iron and lead receive three coats of oxide-of-iron paint. If the chambers are in the open air, one side must be made higher than the other, so that the rain can run away in gutters made for that purpose; but the space between the chambers must be roofed in, so that they can be charged or discharged without any interruption arising from the weather. The plan of placing the chambers in the open air is, however, not to be recommended, and on the Continent,

where the changes of temperature are greater, it is altogether impracticable.

Leaden or iron chambers have this advantage over brick or stone chambers, apart from their larger size, that they better carry off the heat generated in the formation of bleaching-powder, and thus accelerate the work without the danger of spoiling the bleach by overheating.

Bleach-chambers are usually placed level with the ground ; but frequently they rest on *pillars*, with longitudinal sleepers, joists, and flooring, just like vitriol-chambers, leaving an open space of 10 feet high beneath. This space may be used for storing bleach in casks, or lime &c. ; but its principal use is to avoid the most unpleasant work in this manufacture, packing into the casks inside the chamber. In this case there are several trap-doors in the chamber-floor, each with a wooden hopper attached underneath, from which a canvas tube hangs-down, going straight into a cask

Fig. 146.



placed below; through these tubes the finished bleach is pushed down into the casks by means of wooden rakes. (Sometimes stuffing-boxes are provided, in order to employ such rakes for turning over the lime in the absorption-process itself; but these seem now to have been abandoned entirely.)

The arrangement above described, which can be highly recommended, is shown in fig. 146. It has been noticed that bleach packed in this way shows  $\frac{1}{2}$  to 1 per cent. less than that packed inside the chambers; but it loses so much the less on lying. This can be explained thus:—The larger motion of sliding down into the casks only causes the loss of the most easily decomposed portion or of mechanically absorbed chlorine gas.

All bleach-chambers must have some arrangement for *introducing the gas*. This is always in the roof, and generally consists of a water-lute, into which a movable branch pipe can be put from a water-lute of the main gas-pipe. There ought also to be separate connecting-pipes with water-lutes for conveying the gas from one chamber to another. For regular work at least three chambers ought to form a set—the fresh still-gas passing into a nearly finished chamber, the excess-gas into a freshly charged chamber, and, if there are four chambers in the set, again into the third chamber. One chamber is always cut off—that in which the finished product is being packed, or which is in course of being recharged. Neill and Smith proposed an exhauster, which was to convey the gas from one chamber to the other; but this is quite unnecessary.

Sometimes the single chambers are combined with each other in such manner that the entrance-openings are in the top of the chamber at one end, and the exits near the bottom at the other end. This seems to compel the gas to take the most advantageous course through the chamber, viz. the diagonal. But this arrangement, although recommended in Frémy's 'Encyclopédie,' vol. i. 2, p. 75, is quite wrong. The chlorine does not drive the air before it in the direction shown by a diagonal line, but it sinks down to the bottom immediately after entering, as can be clearly observed through the "sights," partly on account of its high specific gravity, partly in consequence of being absorbed by the lime and thus always drawn downwards. Thus the air is not forced out diagonally, but, on the contrary, towards the top of the far end. If the gas near the far end is examined,

Fig. 147.



Fig. 148.

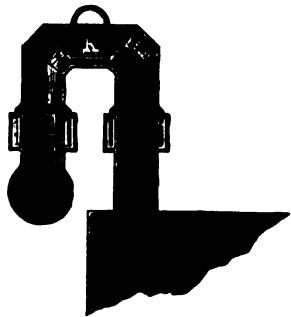
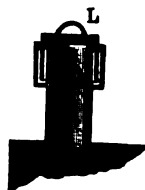


Fig. 149.



the upper layers show least chlorine. Therefore the exit-openings should also be placed in the chamber top, which is also far more convenient for arranging the gas-mains and the hydraulic lutes. Fig. 147 shows how the gas-mains can be arranged in a simple manner, so that the gas can be conducted through the chambers A, B, C in any desired way. The chlorine arrives from the stills by the pipe D, which is provided with a water-lute branch for each chamber, *a, b, c*, to which other lutes, *d, e, f*, correspond in the chambers. The functions of the connecting pipes E, F, G, H, placed on top of the chambers, and of the lutes *g* to *r*, will be made clear by the following description. Suppose chamber A to contain almost finished bleach, B an intermediate product, and C fresh lime, the work will proceed as follows :—Lutes *b* and *c* on the chlorine main are closed by caps ; *a* is connected with *d* (fig. 148 shows how two lutes are connected by a U-tube K ; fig. 149 the closing of a lute by a cap L). The gas issuing from A travels by *g, o, G, p*, and *h* into chamber B, from this at the other end, by *e, m, F, n*, and *f*, into chamber C, and from this, now fully deprived of chlorine, through *i* into the open air. When the contents of A are ready for packing, *a* is closed, *b* is connected with *e*, in order to carry the fresh chlorine into B, and the gas now travels by *h, q, H, r, i* to C ; from here, after A has been discharged and recharged with fresh lime, by *f, n, F, m, l, E, k, d*, to A, and by *g* into the air. Last of all the fresh gas is first passed through *c* and *f* into C, then through *i, r, H, q, p, G, o, g* into A, through *d, k, E, l, e* into B, through *h* into the open air.

Jahne (Dingl. Journ. cclxiii. p. 387) describes the work with a set of four chambers, but the only interesting point in his paper is that the chamber charged with fresh lime is brought to 7 per cent. available chlorine by displacing the chlorine from the finished chamber, while the percentage of the intermediate chambers does not rise to any extent until they receive fresh chlorine from the stills.

*The charging of the chambers with lime* is effected in the following way :—A 3-inch or 4-inch layer of hydrated lime is spread over the floor and levelled ; deeper layers cannot be converted into bleach all through. In some places, and generally in Germany and France, the layers are made less deep, 2 inches or even 1 inch ; this enables the bleach to be finished in one operation, without turning over. On the other hand, where the chambers are worked in sets

the layers can be made deeper (see below). In order to assist absorption, the surface of the lime is "drilled" into furrows by means of a wooden tooth-rake, fig. 150. The lime at the top of the ridges lies about 5 inches, at the bottom 2 or 2½ inches deep.

Fig. 150.



The doors are now put in, and all joints plastered with lime-putty, sometimes with the addition of a little salt. Wet clay, which is occasionally used, is less cleanly. Clay is best worked up with a solution of calcium chloride to keep it always damp and prevent the formation of cracks. It is also a good plan to paste up the joints with paper and flour-paste.

The *treatment with chlorine* ("gassing") is of course different according to whether each chamber is treated separately (as was formerly the universal plan in England), or the chambers are worked in sets, as described above, and as practised for many years past at a number of works.

In the former case the chlorine-gas is introduced from the top of the chamber, mostly in the centre, but a small air-hole in one of the doors is left open, about 5 feet from the bottom, and this is only closed when chlorine issues from it. At first the absorption of chlorine takes place very rapidly, as can be observed through the glass "sights"; the gas entering at the top at once sinks to the bottom, and its green colour vanishes there. If the air has been allowed to get out, there is little fear of any escape of chlorine at this stage. But in time the lime is so far saturated, at first superficially, that it does not absorb the gas so greedily. Some pressure must now be applied to arrest the absorption; and of course special care has to be taken to keep the joints of the doors &c. tight; but, above everything, the steaming of the stills, which always causes a greater pressure in the chambers, must not be overdone. Besides, too much steaming carries, in spite of long pipes and collectors, steam and acid into the chambers, where they do much harm by forming calcium chloride and damp lumps; the heating of the chambers by the warm gas is also very injurious. Steam of moderately high pressure (say 40 to 50 lb. to the square inch) is preferable to weaker steam for the stills, because there is less condensation of water from it.

The work at this stage is very much facilitated if one chamber is kept ready charged with fresh lime, into which the excess of

gas from the first chambers can be carried ; then there is much less fear of gas breaking out.

The glass windows are an excellent means of controlling the process, which no one who has been accustomed to them would like to be without. When the chamber becomes very green, no more gas is admitted into it, and a few hours are allowed to elapse, to see whether it still absorbs the gas contained in it. If this is done within a short time, a little more gas must be admitted ; but if it takes 12 hours or more before the chamber becomes pale, it is time to open it.

Usually it takes 24 hours before a chamber takes up all the gas it can.

The *style of work with a set of chambers* (p. 453) is from the outset easier and less unpleasant than that which has been just described, because it is done *without any pressure*. The fresh gas always goes into the chamber which has been longest at work ; the excess of gas by itself goes into the next, much less saturated chamber, and the air escaping from this must pass through a third chamber charged with fresh lime, where the last of the chlorine is absorbed, so that this chamber can communicate with the outer air. This not merely avoids an injurious pressure on the joints of the chambers, but it also puts much less strain on the lutes of the stills themselves, where with the one-chamber system it happens not unfrequently that chlorine blows off—one of the most unpleasant incidents in alkali-works.

In the three-chamber system it is possible to work with higher layers, up to 8 inches deep, and to obtain quite as strong bleach as with the lower layers in the one-chamber system.

[This system, already described in our first edition of 1880, vol. iii. p. 163, as the *only rational one*, is mentioned in the 22nd Alkali Report (for 1885), p. 8, as a novel, most important improvement brought out in a large English alkali-works, by which it had been rendered possible to make stronger bleach than previously, to lose no chlorine, and to cause no nuisance.]

The *opening of the chamber-doors* was formerly one of the most awkward operations in alkali-works, by which an intolerable nuisance was caused, not merely within the factory, but sometimes at a distance of a mile or two. Where the chamber-space was not too limited, this drawback could be lessened by allowing each finished chamber to stand over-night, so that the free

chlorine could be absorbed by the bleaching-powder at the bottom; but this was an uncertain and always imperfect remedy, and even then other measures were taken at some works for reducing the nuisance, which are now quite universal.

About 1884 the English Alkali Inspectors, on account of the numerous complaints about this nuisance, made investigations which showed that, for instance in the Newcastle district, the air issuing on opening the chamber-doors contained, on an average, 12 grains chlorine per cubic foot, but sometimes up to 100 grains, while  $2\frac{1}{2}$  grains is the limit, above which the escaping air causes a considerable nuisance even at a distance. By an amicable understanding with the manufacturers it was agreed that  $2\frac{1}{2}$  grains should be the upper limit of the amount of chlorine in the chamber-air before opening the doors. But evidently this could not be carried out, for by an official circular, dated November 1st, 1886 (23rd Report, p. 13), a limit of 5 grains per cubic foot was established, above which the factories were to be legally prosecuted, which, however, was not found necessary in a single instance.

The inspectors test the chamber-air for chlorine by means of a solution of potassium iodide and sodium arsenite, with addition of calcium carbonate, through which the air is injected by means of a finger-pump, until the appearance of a colour shows the presence of more chlorine than can be oxidized by the arsenite. The apparatus employed is shown in fig. 151. A is an india-rubber squirt, holding 4 ounces (about 100 c.c.), in the nozzle of which a small hole, B, is drilled; the end of this tube, as well as a bent glass tube D which reaches almost to the bottom of cylinder E, passes through the cork C. The lower end of D must be narrowed up to the point so that only a fine needle can be introduced. E is filled with the test-solution to be described below. The outer end of D is put into a hole in the chamber-side, about 2 feet from the bottom, the ball A is squeezed with the hand as tightly as possible, hole B is closed with the finger, and the pressure on A is released. By the expansion of the india-rubber ball, the apparatus must aspirate chamber-air through D and through the liquor contained in E. When this operation is finished, it is again performed, and this process is repeated until the liquid in E shows a colour, the operator taking note of the number of charges of the ball A. Each charge



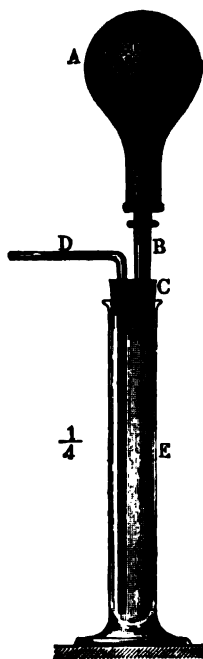
= 4 ounces, and is  $= \frac{1}{250}$  cubic foot. A solution indicating  $2\frac{1}{2}$  grains per cubic foot with ten aspirations (or 5 grains with five aspirations) is prepared as follows, according to the 22nd Report, p. 54, translating grains into grams:—0.3485 gram arsenious acid, dissolved in sodium carbonate and rendered neutral by sulphuric acid; 25 grams potassium iodide; 5 grams precipitated calcium carbonate; 6 to 10 drops ammonia—the whole being diluted in 1 litre of water. For each test 26 c.c. is used, adding a little starch-paste.

Fleming Stark (Journ. Soc. Chem. Ind. 1885, p. 311), instead of the just-described chlorometer, employs an Orsat apparatus, but any other gas-analytical apparatus may be used.

The simplest plan for avoiding the nuisance by escaping chlorine is to put the chamber in communication with a tall chimney before opening the door. For this purpose the chamber is provided at one end, a little above the bottom, with a side-tube, ordinarily closed, which can be connected by a leaden or earthenware elbow-pipe with an underground flue leading to the chimney; at the same time the lute in the opposite end of the chamber-roof is opened. Fresh air will enter here, and push the gas within the chamber towards the chimney. If, however, the chimney is not very tall and wide, and does not carry much fire-gas from black-ash furnaces, &c., the chlorine gas escaping through it, although not causing any nuisance at the works themselves, will do so at some distance. In this case a lime-tower or similar contrivance ought to be interposed in the flue; this is troublesome, and does not yield any useful product, but otherwise it answers the purpose very well.

Much more rational, and at the same time more economical, is the displacement of the gas in a set of several chambers working together. Here simply the last chamber, that is that which is charged with fresh lime, is put in communication with a chimney, or, failing this, with an injector, before opening the air-inlet of

Fig. 151.



the first chamber, containing the finished bleach. The fresh air entering here will force the gas containing chlorine into the second chamber, and from this into the last, without any chlorine being lost or any smell being caused, as the fresh lime in the last chamber retains everything. It is very advisable to conduct the fresh air first through a small leaden tower fed with a little sulphuric acid of 144° Tw., in order to dry it; this avoids the diminution of the strength of bleach by the moisture of the air, which otherwise occurs. The passage of the air must sometimes be continued for 12 hours, to remove all chlorine from the chambers; but with exit-pipes 15 to 18 inches wide much less time suffices.

The English inspectors were after all not quite satisfied with the above-described proceedings, because sometimes the chambers were opened in a hurry, before sufficient time had elapsed for the gas to be drawn through a freshly-charged chamber. They therefore recommend *sprinkling lime-dust* into the chamber through the top. This had formerly been practised at some places, but merely by hand, and therefore incompletely and irregularly. The object in view is completely attained by the apparatus of Brock and Minton (pat. No. 7199, 1886), which is recommended by the inspectors as excellent and found efficient at several works. It is shown in figs. 152 to 154. A is a funnel for lime-dust, B a valve for regulating the feed; D a fan for sprinkling the dust about in the chamber; E gearing for setting the fan in motion, which can be done by hand: the whole is enclosed in a box, except the lowest part which is within the chamber. Near D is an opening for letting out the dust into the atmosphere of the chamber. Eight iron pipes F serve as stays for the machine, with openings just below the chamber-top; this assists in mixing the lime-dust with the chamber-gases, as during the revolutions of the fan air is drawn in through F and expelled through. One such machine is placed every 30 feet of the length of the chamber, and is adapted to a corresponding hole by a flange H.

By means of this machine the chlorine in the chamber atmosphere can be reduced to 1 grain per cubic foot, and yet strong bleach, testing 37·5 to 38 per cent., is obtained. For a ten-ton chamber about 4 cwt. of lime is used and 6 cwt. more bleach is obtained.

The same object is attained by Mooney, who allows the hydrated lime to fall down in a funnel which at the bottom turns off at a

right angle; here it issues through a  $\frac{1}{8}$ -inch hole and is projected into the chamber by a jet of compressed air, in the shape of a cloud.

After opening the doors the contents of the chamber are

Fig. 152.

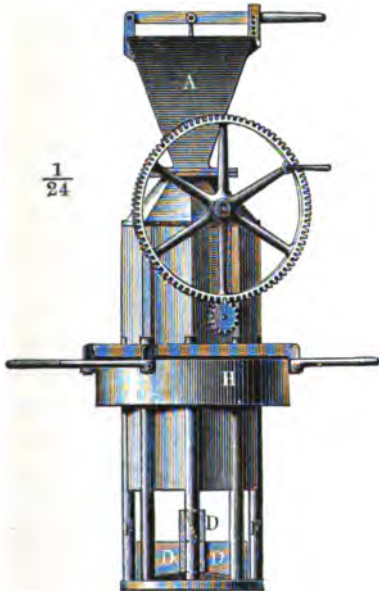


Fig. 153.

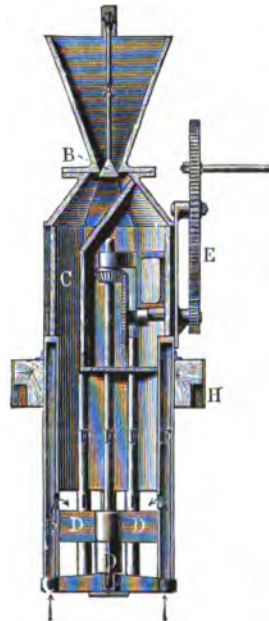
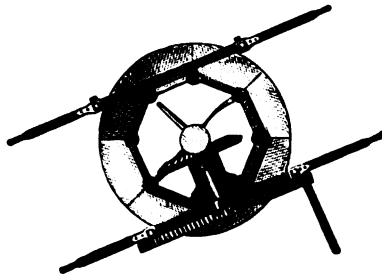


Fig. 154.



examined at once. In any case there will be a superficial crust of bleach; but only with very shallow layers (2 inches) is it possible to get 35 per cent. bleach in one operation.

Testing in the laboratory affords certainty in this respect; but the workmen can judge pretty well by empirical tests whether the bleach is finished or not. The product ought to consist of pretty heavy flakes, not floury, but easily crushed. When a little is taken up on a shovel and thrown off, the powder ought to fall down heavily, not in clouds of dust, which are caused by lime. Kneading a well-mixed sample with the fingers ought to make it tough; it will do this only to a very good, strong bleach, which, however, cannot be expected the first time; the bleach at this stage generally tests only from 25 to 30 per cent. available chlorine.

In order to make strong bleach, the contents of the chamber must be turned over with the spade, all lumps crushed, and the stuff lying on the bottom turned upwards. The surface is again dressed into furrows (drilled), the doors are closed, and gas is admitted again. An attempt has been made, but unsuccessfully, to avoid the opening of the doors, by working the rakes for turning over the lime through stuffing-boxes. What we have said above about the care necessary in saturating with chlorine holds good here in a higher degree. When the chamber absolutely refuses to absorb any more gas, the latter is cut off, the chamber allowed to rest for 12 or 24 hours to give it a chance of absorbing as much gas as possible, and then opened with the same precautions as the first time. As a rule, unless there has been some neglect, the product is now found strong enough for packing—testing at least 36 per cent., as there is always some loss of strength in packing and sampling. But if badly chosen, badly burnt, badly slaked or sifted lime has been employed, if the manganese ore contains carbonates, if there has been too much steaming and hence sensible quantities of HCl and water have got into the chamber, no strong bleach need be expected. If the strength is found to be only 33 or 34, or even 35 per cent., it will be necessary to turn the stuff again, close the chamber, and give it a little more gas; but if the third time the strength has not got up to 36 per cent., the powder must be packed as it is and sold for what it will fetch; for if a batch saturated with chlorine according to the circumstances is treated with fresh chlorine for some time, it goes back in strength, and that considerably. Some workmen think to remedy this by mixing some fresh lime with the powder before admitting fresh gas; I have never seen much success from this,

but I have several times got rid of a chamber of 33 or 34 per cent. by bringing another one by special care up to 38 or 39 per cent., mixing the contents of both, and packing them together.

In England the bleach is packed as it is; but in France it is usually deprived of lumps by sifting; in this operation it will probably lose a little strength, but will keep all the better afterwards, because it cools completely (see below).

The whole time elapsing from the charging of a fresh chamber to its being emptied by packing the finished bleach is about a week.

To obtain the best strong bleach, *the gas must be passed in slowly and gradually*. The slower the better is a practical rule; lofty chambers in this respect act better than low ones, because the newly-arriving chlorine-gas is always getting mixed with the old chamber-air before reaching the lime. Attempts made in the same chamber at passing in the gas, in one case near the top, in the other near the bottom, have shown that the strongest bleach was obtained in the first case. Evidently this bad effect of introducing the chlorine too quickly and allowing it to act almost directly on the lime is caused by *too great a rise of temperature*. During the absorption of chlorine by lime much heat becomes free; under favourable conditions, according to Morin, the temperature rises to  $119^{\circ}\text{C.}$ , in which case undoubtedly much chlorate is formed. Berzelius declares even a temperature of  $20^{\circ}\text{C.}$  to be unfavourable for bleach-making; but this seems exaggerated. Scheurer-Kestner (Compt. Rend. lxx. p. 894) found that occasionally the highest temperature is generated in the top layers, but sometimes the contrary is the case. He affirms that temperatures up to  $55^{\circ}\text{C.}$  are suitable for making strong bleach. With a large excess of chlorine the calcium hydrate gets heated up to  $80^{\circ}$  or  $90^{\circ}\text{C.}$ ; but the product is then already partially decomposing. He asserts that he has found the highest percentage of chlorine in the warmest ( $55^{\circ}\text{C.}$ ) places, and hence considers a certain rise of temperature favourable to this process. According to observations made by myself and Schäppi (p. 425), a temperature of  $40^{\circ}$  to  $45^{\circ}\text{C.}$  is the best for the production of strong bleaching-powder.

In 1877 (Feb. 6) Cook applied for an English patent for heating the chambers or chlorine-pipes by steam; but even provisional protection was refused for this. According to general experience, the practice of manufacturing on a large scale shows that bleaching-powder is all the better the cooler the chambers can be kept.

For this reason lead chambers are superior to stone chambers; and from the same cause it is notoriously much easier to make strong bleach in winter than in summer. In France, on account of the warmer climate, at least in summer, no stronger bleach than that containing 30 or, at most, 32 per cent. of available chlorine is made.

This apparent contradiction is probably explained by the fact that immediately above the most favourable temperature for the production of chloride of lime the critical point sets in where chlorate is formed, and that on the large scale it is not so easy as in the laboratory to keep the temperature exactly at that limit, so that we must keep considerably below it in order to be on the safe side.

Agreeing with this is an observation made by Mr. Benker, formerly manager of the Petit-Quevilly works near Rouen, who informs me that, in order to avoid a rise of temperature and too much moisture, he mixes his (Weldon) chlorine with 50 per cent. air, by means of an air-pump, previous to allowing it to act on the lime. In this case no hard crust is formed on the lime, and the operation proceeds very regularly and smoothly. The strength of the bleach on introducing the new system suddenly rose from 35 to 38 per cent., at which point it was regularly kept. Probably, besides the reasons mentioned by Mr. Benker, the dilution of the chlorine with air would check the formation of chlorate.

It is also certain that, when the chlorometrical test of bleach has reached its maximum, it is reduced by any excess of chlorine gas admitted to it. We have treated, on p. 420, of the decomposing action of chlorine on bleach and on hypochlorites respectively. Scheurer-Kestner proved by a series of experiments that the top layer of bleaching-powder in the chambers, which is in immediate contact with the gas and should be richest in chlorine, always tests less than the layer immediately below. This, however, may be partly caused by the fact that any HCl carried over would be retained in the top layer. I once found that 33-per-cent. bleach, which was to be brought up to strength by an excess of chlorine, came down to 27 per cent. The investigations of Hurter on the absorption of chlorine in the Deacon process (p. 406) should also be compared here.

The observation quoted, p. 463, according to which weaker bleach is produced by admitting the chlorine directly to the lime, is confirmatory of all these considerations.

According to Opl (Engl. pat. 4984, 1882) a lime surface of 1 sq. metre and 1 metre high (=500 kil.) at a pressure of 32 feet water absorbs 57 kil. chlorine per hour; it would thus take 4.3 hours to absorb the requisite 250 kil., but this is not feasible on account of the evolution of heat. The latter must be rendered harmless, either by cooling or by dilution with air [which was practised long before, and published in our first edition, vol. iii. p. 270]. Opl's chamber has a double bottom made of two layers of laths of wood soaked in linseed oil, with canvas between the layers. The drawing-out of the air and forcing through of the chlorine is performed by a water air-pump, the water being at the same time employed for cooling, by allowing it to run on to the chamber top, from which it flows down the sides and runs away in a spout above the cast-iron bottom. The chlorine is forced in at the top, and the process is finished when it appears below the grating. In order to make the very strongest bleach, the chlorine must be first purified in a separate box by means of ground, unslaked quicklime, employing 2 to 4 per cent. lime-dust of the same weight as the bleach. By means of this apparatus it is contended that a layer of lime ten times as thick as usual can be employed, and no chlorine is lost.

Solvay (Engl. pat. 839, 1880) moulds the slaked lime into balls and exposes these to chlorine in an upright cylinder.

The *difference in strength* between an average sample drawn from the chambers and one taken from the casks is partly caused by a loss of chlorine, principally that which had been merely mechanically retained in the interstices between the particles of bleaching-powder; partly by the absorption of moisture during the mixing and packing, which of course causes an increase of weight. This difference in strength on an average amounts to 1 per cent.

*Mechanical bleaching-powder chambers.*—Many other forms of absorbing-apparatus for chlorine have been tried, but unsuccessfully until quite recently, apart from the Deacon chambers for dilute chlorine (p. 404). Already in 1816 (according to Richardson and Watts, iii. p. 375) Oberkampf and Widmer proposed revolving cylinders; and this is said to have been the first plan of manufacturing bleach in Germany. It is represented in the sketch fig. 155. The cask A was two-thirds filled with hydrated lime; the chlorine gas entered through the perforated pipe *d*, into which the smaller

pipe *e*, coming from the stills, was cemented. The cask rested on the bearings *a* and *b*, and was turned round by a handle at *c*. Another arrangement is said to have been carried out in England, as shown in figs. 156 and 157. A A A are cylinders of  $\frac{1}{4}$ -inch sheet iron, 5 feet in diameter and 13 feet long, coated with cement inside; at one end they have man-holes B B, and are fixed on a wooden frame at such elevation above the ground-floor that the bleaching-powder from them can fall into the packing-casks through a sieve. The axles C C C are hollow and perforated, so that the gas can enter the cylinders; it comes from

Fig. 155.

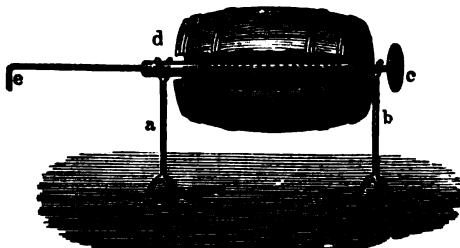
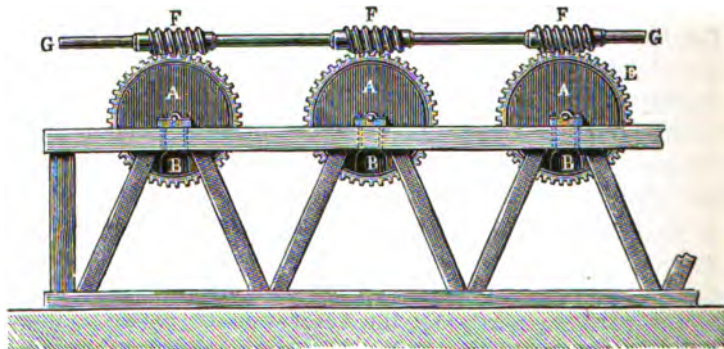


Fig. 156.



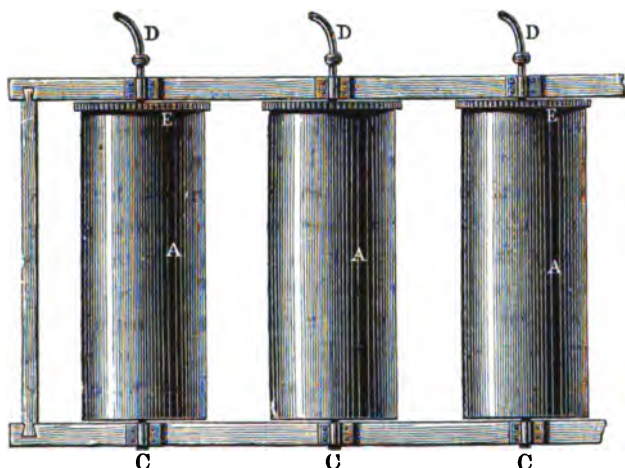
the stills through the pipes D D D. The cylinders are made to revolve by the cog-wheels E E and the endless worms F F on the main shaft G. By shifting the worms F F each cylinder can be thrown into or out of gear. The revolutions are slow, 12 or 15 per hour. Each cylinder is charged with about 14 cwt. of calcium hydrate. (Evidently the lime gets too hot in this case, and weak bleach is the consequence.)

The manufacture of bleach by dropping lime down a tower or shaft in which chlorine-gas ascends has been proposed several times, *e. g.* by Larkin, Leighton, and White (patent No. 1357, 1871), and Leather (No. 2308, 1871), especially for chlorine



diluted with air; also by Bramwell (No. 2962, 1871) and Hargreaves (No. 5001, 1876). Bramwell's apparatus has an agitating-shaft inside; Hargreaves's is a vertical cylinder with horizontal shelves, down which the lime is slowly conveyed by means of a central revolving shaft, carrying horizontal arms and scrapers; the lime arrives as finished bleach at the bottom. Cold water circulates in the double walls of the vessel and in the hollow agitator. The apparatus resembles McDougall's pyrites-burner (Vol. I. p. 260) and Solvay's soda-drying apparatus (Vol. III. p. 82); Kellner's apparatus (Engl. pat. 20037, 1891) is similar.

Fig. 157.



Similar to the last also is Kopfer's apparatus (Germ. pat. 9398), consisting of an octagonal chamber 13 feet high, from the top of which the lime is sprinkled about by means of a centrifugal drum with 600 to 1200 revolutions per minute, covered with a wire gauze of 5 millimetres width of meshes. Fehres (Germ. pat. 24702) introduces the lime by an Archimedean screw and injects it into the chamber by means of compressed air. W. J. and L. M. Fraser (Engl. pat. 20055, 1892) employ an upright chamber, in which the lime is continually raised by a chain of buckets and thrown upon fixed inclined planes. Platt (Engl. pat. 728, 1867) describes a tower with slanting shelves, mechanically shaken, attached alternately to opposite sides.

The apparatus of Riddel (No. 2316, 1875) and Malétra (No. 3547,

1877) are pretty much the same thing. Malétra employs a horizontal wrought-iron cylinder, 13 feet long and 6 feet wide, with doors in the sides and below; a central shaft with spirally placed arms and iron blades 10×6 inches wide turns the lime round 12 or 20 times per minute. The chlorine-gas enters at the top. There are two openings for allowing the "heat and moisture" to escape [?]. A thermometer serves for controlling the process; in summer an excessive temperature can be avoided by a water-jacket. The finished product falls through the lower door into a bogie. Such a cylinder is stated to turn out a ton of bleaching-powder in 24 hours. The inventor claims as advantages of his process speed of manufacture and uniformity of the product. (This apparatus, from my own knowledge, has been at work for a very short time.)

Langer (Germ. pat. 39661) arranges within a trough two parallel conveying-screws, turned opposite, the screw-blades interpenetrating as much as possible, but without touching.

All mechanical bleaching-powder chambers hitherto erected have been abandoned after a short period of work, either because the machinery failed or because the bleach came out weak, or both. Hasenclever's apparatus, however (Engl. pat. 17012, 1888), has been successfully at work already for a number of years; it is shown in figs. 158 and 159. It consists of several superposed tubes (A, B, C, D in the diagram), of which any desired number can be employed in a set. Each tube is provided with an agitator, moved by a spur-wheel at one end of the axle, and at the same time serving as a conveying-screw. The axle of the bottom agitator receives the motion from the gearing by means of an endless screw and transmits it by a spur-wheel to the agitators above. The screw-wheel S is loose upon the axle and is connected with the spur-wheel by a pin T, if the agitator is to be set in motion. If T is removed, the whole apparatus is stopped. The lime is charged through the hopper E, moved forwards by the top agitator to the other end of tube A, and falls through F into tube B. Here it is conveyed backwards to the other end, and falls through G into C. In the same manner it is again conveyed forwards in C and backwards in G, and at last arrives as finished bleaching-powder in the collecting-box I, from which it falls through a slide into the casks.

Fig. 158.

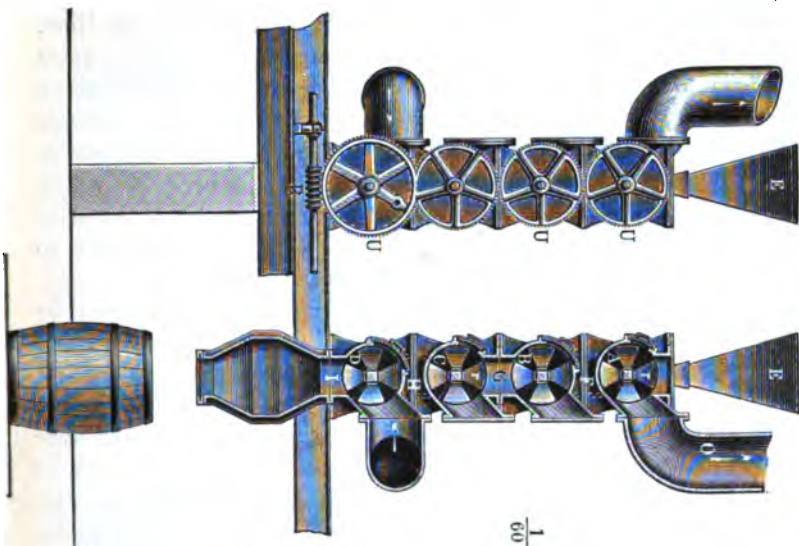
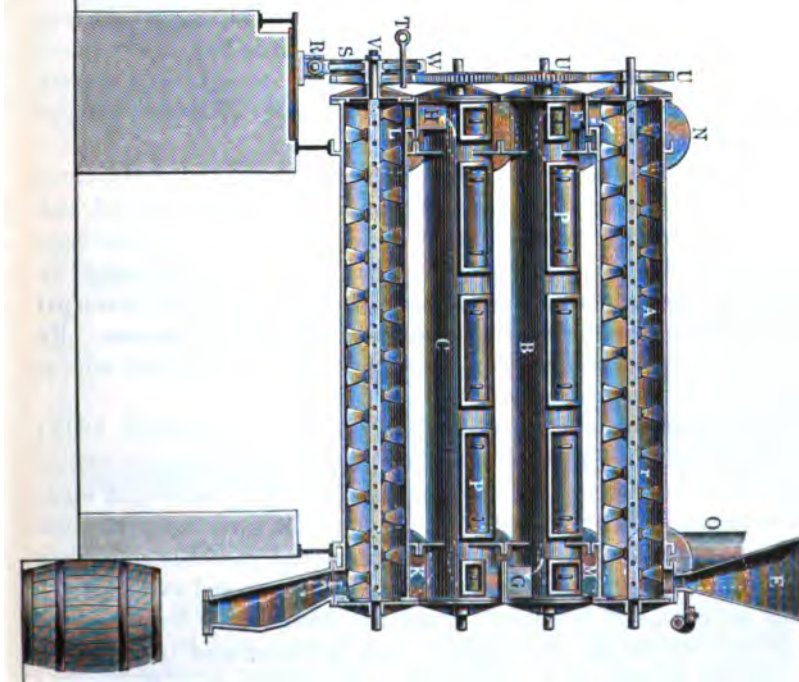


Fig. 159.



The chlorine gas travels in an opposite direction to the lime. It enters at K in D; from there it travels by H into C, and from there upwards by the branches G, F, which serve for the dropping of the lime, into the higher tubes. At first the gas-channels were placed laterally, to avoid carrying along much lime-dust, but this has been found unnecessary. The hopper E, which receives the sifted lime, is closed at the bottom by a throttle-valve, opened and shut by a cam fixed on an axle, in order to produce a uniform and regular charging of the lime.

The working of the conveying- and agitating-screws can be observed through openings in the tubes A, B, C, D, tightly closed by caps P; these admit of inspecting the inside of the tubes and cleaning them in case of need. The blades of the agitators are made very broad at their outer ends, so as to move and turn over as much lime as possible, and present constantly fresh surfaces to the chlorine. The moving power for four agitators is = 1 H.P. The cost (at Aachen) is about 7*d.* per ton of bleach, including the slaking and sifting of lime, superintending the apparatus, and packing the bleach. A four-tube apparatus furnishes about a ton of bleach per diem. The advantage consists less in a reduced cost of production than in the diminished trouble and injury to health caused to the men by breathing bleaching-powder dust and chlorine-gas.

At first the apparatus failed to work with concentrated chlorine; the lime became too hot, and the product was decomposed and came out mostly as calcium chloride. Since then it has been found possible to make good bleach from strong chlorine by working the apparatus only intermittently; but its principal application is for the weak chlorine from the Deacon process. By mixing air with the chlorine, as mentioned pp. 464 and 465, it would probably work as well with strong gas.

The apparatus of J. M. and A. Milnes (Engl. pat. 15833, 1891; 19180, 1892; 21356, 1893) is constructed on a principle similar to that of the drying-machines employed in the bleaching of wool. It is shown in figs. 160 and 161. Each of the three compartments of a chamber, built of slate or similar material, contains an endless cloth D, made of asbestos tissue, which has proved excellent for this purpose, and is turned round the drums E, E by means of the spur-wheels K, K. Slaked lime is introduced in regulated quantities by hopper A and feed-valve B; it falls on to the endless

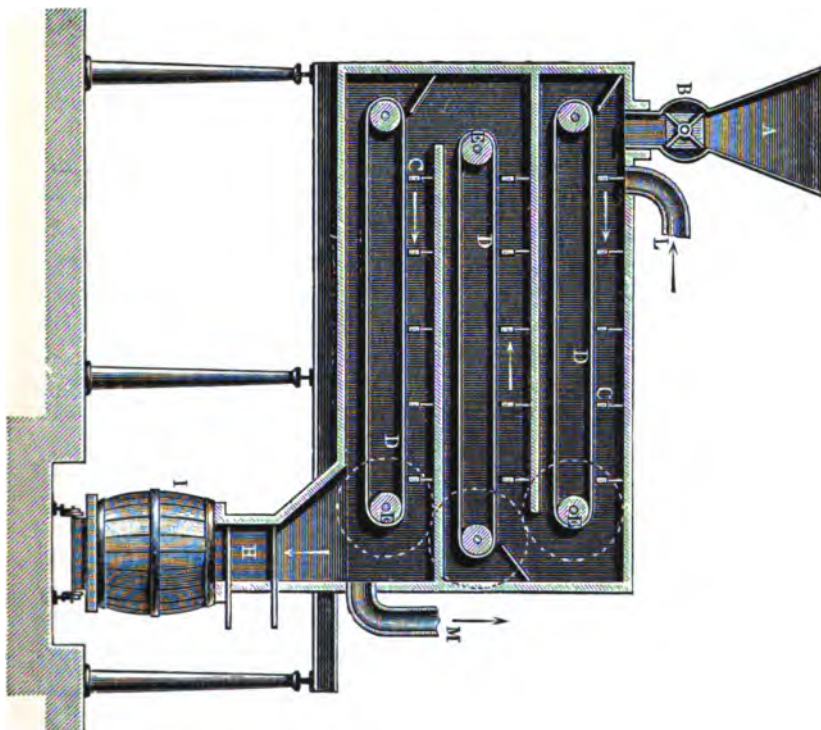


Fig. 100.

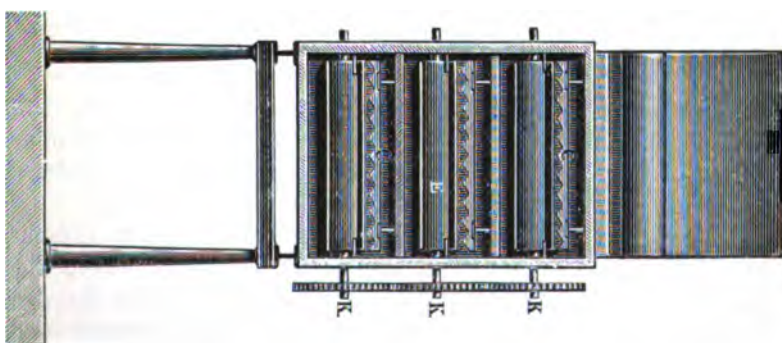


Fig. 101.

cloth and travels along with it through all three (or more) compartments of the chambers till it drops through H into cask I. The undulated combs C, C, suspended from the ceilings of the

compartments, constantly turn over the lime. The chlorine gas enters at L together with the lime; it is drawn through the apparatus by an exhaustor and leaves it at M.

*Dilute chlorine gas*, such as is made not merely by the Deacon process, but also by many of the processes starting with calcium or magnesium chloride, &c., is treated in the first instance by the chambers constructed by Deacon himself (p. 404), as well as by several of the mechanical apparatus mentioned, especially Hasenclever's. We will here mention an apparatus of Solvay's (Engl. pat. 7259, 1885), who puts into his chambers grids of open mineral substances, like pebbles or asbestos cloth, upon which the lime is spread; the chlorine is conveyed through them from the bottom upwards, not *vice versa*. [These grids quickly become clogged on discharging the bleaching-powder.]

#### *Packing the Bleaching-powder.*

Since in no case are all the layers of bleaching-powder of one uniform quality, account must be taken of this on sampling, and still more on packing. The contents of a chamber should be very well mixed, the whole put into a conical heap in the centre of the chamber, and left to itself with closed doors, till the rise of temperature taking place on mixing the different layers (comp. p. 480) has entirely vanished. This heating is produced by the varying percentage of different layers, and it may amount to 20° C. Packed in this way, the bleach is more durable than when packed immediately after mixing up. Bleach which has been exposed to the rays of the sun before packing is said to keep very badly afterwards. Observations on the decomposing action of the rays of the sun have been made by Riche and by Bobierre (Compt. Rend. lxx. pp. 59 and 803). It is easily explained by the combined action of heat and light, such as has been observed, for instance, in the experiments made by myself and Landolt (p. 438).

In order to pack the bleaching-powder, as made in ordinary chambers, the men must go inside the chambers, where they have to shovel it together and mix it up. In the case of chambers erected on the ground floor they have also to fill the casks inside the chamber. The latter part of their task is a comparatively easy and not over-harassing kind of work where the chambers are placed upon pillars, as shown p. 452, and the packing is performed outside, that is underneath, the chamber; and there is

even less trouble in the case of mechanical chambers, p. 468 *et seq.* But in the ordinary chambers, even after clearing them of gas as mentioned on p. 459, it is work of the most unpleasant and unhealthy description, the men being harassed not merely by the gaseous chlorine, imprisoned by the powder and being set free as the powder is moved, but also by the fine dust of the powder itself with which the chamber-atmosphere is charged. In England the men protect themselves by a "muzzle," that is 20 or 30 layers of damp flannel, tied over the mouth, the nose remaining free; they inhale the air through the muzzle and exhale it through the nose. The flannel must not be either too damp or too dry; it is best simply wrung out by hand after washing. The English Chemical Works Committee of Inquiry of 1893 recommends moistening the flannel from time to time with a solution of sodium bisulphite.

This Commission also recommends to thoroughly carry out the (previously well-known) protection of all exposed parts of the skin by oiling or greasing; also the employment of "goggles" and further protection of the eyes by rubbing them now and then with a few drops of castor-oil. The men generally wrap their arms and legs in several folds of thin brown paper, to prevent the bleaching-powder from getting inside their clothes.

Sometimes large sponges are employed, or respirators made of cotton-wool, or filled with a mixture of slaked lime and Glauber's salts; but the latter do not seem to have answered their purpose. In Germany a sort of helmet is employed enclosing the whole head, and pure air is supplied by bellows from without, thus enabling the men to remain longer in an atmosphere of noxious gases without injury. But it would appear that English workmen cannot be got to employ such measures; even the Commission abstains from recommending them, and contents itself with the "muzzles," improved as above stated. The men can remain in the chambers for an hour, or even a little longer, when thus protected, before they are compelled to seek some relief in the open air for their inflamed eyes and respiratory organs, strained by breathing through the "muzzle"; if the latter becomes dry in the meantime, they are "gassed" nevertheless.

Similar precautions must be employed when turning a chamber (p. 462); also, but to a much less degree, when slaking and sifting and charging the lime.

It seems strange that the breathing of ammonia vapour does not appear to be at all practised as a precaution against "gassing," and is not so much as mentioned by the Commission. I have employed this frequently myself; Jurisch states that he did so with the greatest success in his own case, but could not induce the men to do likewise. This remedy must, of course, be employed with caution, as the ammonia vapour, if too strong, would only further irritate the already inflamed mucous membrane.

Other remedies against "gassing" by chlorine have been already enumerated (p. 264); among these I have myself somewhat successfully employed the inhalation of the vapour of ordinary ether.

The inhalation of chlorine-gas (comp. above, p. 263) or bleaching-powder dust causes a strong irritation of the mucous membranes of the windpipe and the bronchiæ, and consequently violent coughing and expectoration; if repeated, it may lead to bronchitis or asthma, and in bad cases to an affection of the lungs. Spitting of blood, vomiting, and incapacity for taking food are of frequent occurrence. Men suffering from weakness of the throat or lungs ought to keep away from this kind of work from the outset. Inflammation of the eyes (conjunctivitis) is frequently induced. Jurisch mentions that the action of chlorine causes the sensation of heat upon the skin, and that the men speak of the chambers being insufferably hot when the temperature is only about 25° C.; but this may be due to a confusion of the various meanings of the word "hot." Real burns are caused by chlorine on sore places of the skin, or such covered with perspiration, and the greasing is merely employed as a protection.

Experienced men, when they have to step into a bleach-chamber containing gas, or when they are otherwise suddenly exposed to an atmosphere of chlorine, do not try to hold their breath until they are out of it again, for this is often impossible; and when, after all, an inhalation is taken of the noxious gas, it then penetrates into the finest ramifications of the pulmonary tissue, inducing bad pulmonary catarrh. On the contrary, they breathe regularly, but quickly, so that the gas only gets as far as the comparatively less sensitive surface of the bronchiæ.

The remedy commonly used by English workmen to abate the trouble caused by "gassing" is whiskey; but some, more rationally, prefer rest, and, if possible, now and then abstain from this work for several days.

The English Commission strongly recommends the introduction



of mechanical bleaching-powder chambers, especially Hasenclever's (p. 468), as being a thorough remedy for the evil.

*Packages for bleaching-powder.*—The *casks* for bleaching-powder should be made of dry wood; they are mostly lined with brown paper, and hold 5 or 6 cwt. more if limestone than if cliff has been employed. Hard-wood casks are charged for rather higher than soft wood, about 5*s.* per ton more than the latter; they are mostly employed for over-sea carriage. The bottoms are covered with plaster, or at least painted with lime. The casks must be protected both from rain and sunshine; for heating by the direct rays of the sun may cause a sudden, explosion-like decomposition of the bleaching-powder (Hofmann and Kunheim, Wagner's Jahresb. 1860, p. 88; 1861, p. 183). In this case oxygen is set free, and the residue consists chiefly of calcium chlorate and chloride (comp. p. 472). Such cases are extremely rare; but the *slow* decomposition of bleaching-powder in course of time is an unavoidable drawback which will be subsequently alluded to.

In hot countries bleaching-powder keeps a much shorter time in the warehouses than in Europe. In India (Papier-Zeitung, 1894, p. 1511) the warehouses are provided with large gates in the two opposite ends, filled with brushwood, upon which a constant stream of water is run; this lowers the temperature from 5° to 10° C. By this proceeding the strength can be kept even in the hot season for several months at 25 per cent., in the colder season at 27 to 29 per cent. But as soon as a sign of decomposition appears, the bleaching-powder must be used up at once. Boxes lined with lead or zinc offer no great advantage over ordinary wooden casks. It keeps best in iron drums, but these resist corrosion only about two months in the hot, or three to four months in the cool season. As soon as a single iron drum has corroded and allows chlorine to pass, all others are quickly attacked; hence the first drum must be at once removed before any chlorine can escape from it.

Bleaching-powder for carriage to hot countries is sent out in air-tight iron drums, holding 2, 3, or 5 cwt.; for consumption in Europe on the small scale, in laundries, for household and disinfecting purposes, in iron canisters holding  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1, and 10 lbs. Of the smaller canisters 48, of the 10-lb. 24, are put up in a case.

Steed (Engl. pat. 3902, 1881) packs bleaching-powder in boxes made of wood-shavings, paper, or pasteboard, which are pasted up and then soaked in melted wax, paraffin, or the like. Needham

(Eng. pat. 19121, 1890) proceeds exactly in the same manner, but he dips his boxes into boiled oil. Bush (Eng. pat. 799, 1874) contents himself even with paper, soaked in oil or resin.

*Properties of Bleaching-powder.*

Bleaching-powder ought to be a pure white powder, which in the case of a strong article is mixed with lumps; but these on crushing ought to show just the same properties as the powder; they ought to be completely transformed, and not to contain a core of lime. These lumps are sometimes removed by riddling. In the air, bleach gradually attracts moisture and carbonic acid, and finally deliquesces to a pasty mass. It has a peculiar smell, different from that of chlorine, and usually ascribed to hypochlorous acid set free by the carbonic acid of the air; but this, according to Winkler (Dingl. Journ. cxcviii. p. 149), cannot be so, as bleach solutions to which an excess of alkali has been added exhale the same smell, even after boiling and cooling in an atmosphere free from carbonic acid. We must, however, not overlook that Austen found free hypochlorous acid to exist in alkaline solutions (p. 418). Mixed with a little water, bleach forms a stiff paste, with a perceptible rise of temperature; if ground up with more water, most of it enters into solution (according to Fresenius first the calcium chloride), but there always remains a considerable residue, chiefly consisting of calcium hydrate, but always containing some bleaching chlorine, which can only be washed out by a very large amount of water. The aqueous solution has a faintly alkaline reaction, the smell of bleaching-powder, and a peculiar astringent taste. This solution is almost exclusively employed in bleaching, as the residue would contaminate the paper-pulp, the fabric, &c., and even locally destroy them. M. F. Hodges has proved that after complete washing the insoluble residue of bleaching-powder is quite harmless.

[A table of the specific gravities of solutions of bleaching-powder has been given, p. 437.]

*The testing of bleaching-powder* for available chlorine and its full analysis are described on pp. 429 and 438. Analyses of bleaching-powder are, among others, found in Lunge and Schäppi's paper (p. 424). Here we shall merely quote some full analyses given by Pattinson (Journ. Soc. Chem. Ind. 1886, p. 589).

	From Irish limestone.		From French cliff.
	A	B	C
Available chlorine .....	37·00	38·30	36·00
Chlorine as chloride .....	0·35	0·59	0·32
„ chlorate .....	0·25	0·08	0·26
Lime .....	44·49	43·34	44·66
Magnesia .....	0·40	0·31	0·43
Ferric oxide .....	0·05	0·04	0·02
Alumina .....	0·43	0·41	0·33
Manganic oxide .....	trace	trace	trace
Carbon dioxide .....	0·18	0·30	0·48
Silica, &c. ....	0·40	0·30	0·50
Water and loss .....	16·45	16·33	17·00
	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00
	<hr/>	<hr/>	<hr/>
Total chlorine.....	37·60	38·97	36·58

Bleaching-powder *decomposes* gradually, even in the absence of air, as is proved by the instance communicated by Hofmann of the explosion of a tightly stoppered bottle, also in well packed and protected casks—but especially under the influence of air and light. Sometimes the decomposition takes place quite suddenly, but only when warm bleach has been packed in hot summer weather (pp. 472 and 475).

Hurter (Dingl. Journ. ccxiii. p. 432) noticed only once in ten years, with a weekly make of 100 tons of bleach, a case of considerable heating and decomposition of a cask of bleaching-powder, which he ascribes to an accidental admixture of organic substances.

Wright and Kingzett ascribe the explosive properties of bleaching-powder to an admixture of a manganese salt (Chemical Society's Meeting of March 20th, 1879).

The shaking in a railway truck or a waggon also injures it more than quiet lying in a dark dry place. Hence the strength of bleach is nearly always guaranteed only at the place of shipment; but bleach shipped with 35 per cent. in England ought still to show at Hamburg or New York 33 or at least 32 per cent. Pattinson (Chem. News, xxix. p. 143) examined the speed at which bleaching-powder loses its available chlorine. In the course

of 12 months the strength of the following examples of bleach was lowered :—

	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
from	28·7	37·4	37·1	32·9	35·2	36·7	31·8	37·6	37·6
to	20·8	31·2	30·2	22·2	27·9	28·0	26·4	28·2	32·3

The samples A, B, and C were taken from different works, but the three numbers of each letter from the same chamber in different stages of saturation. The average loss of chlorine in the first three months, from February to April, was 0·33 per cent. per month; from June to September, 0·86 per cent. per month; from November to January, 0·28 per cent. per month. The greatest loss occurred in August, viz. on the average 1·4 per cent. per month. The monthly loss of chlorine on an average of the whole year was *in maximo* 0·90, *in minimo* 0·50, average 0·63 per cent. It is very noteworthy that weak (28·7-per-cent.) bleach lost strength quite as rapidly as the strong (37-per-cent.), which contradicts the formerly general assumption. Pattinson's observations were made with samples kept in loosely corked bottles sheltered from direct sunlight; possibly bleach packed in good casks may behave somewhat differently. Dullo (Wagner's Jahresb. 1865, p. 253) showed that bleaching-powder continually gives off oxygen, at a lower temperature slowly and gradually, at a higher one quickly; but his suggestion (impracticable in any case) that no bleach should be made above 30 per cent., is shown to be useless by Pattinson's experiments.

Even more important are experiments made by Pattinson later on (Journ. Soc. Chem. Ind. 1886, p. 587). He kept three full-sized casks of bleaching-powder in a well-closed cave, the temperature of which varied during a year from +3° to 17° C. Every month samples were taken and analyzed. At the same time samples of the same bleach were put up in glass bottles, and analyzed at the commencement and end of the whole period of testing, which lasted eleven months. The final results are subjoined. The loss of available chlorine was quite gradual, and amounted at the end of eleven months to the following percentages :—

	In the casks.		In the bottles.
	a.	b.	
A.....	3·20	2·40	2·30 per cent.
B.....	3·10	2·46	1·80 „
C.....	3·10	2·10	1·80 „

Letters A, B, C refer to the analyses given, p. 477. Column *a* shows the loss of strength in the casks as directly found, column *b* that which is found if the increase of weight by absorption of moisture and  $\text{CO}_2$  is taken into account. When doing so, there is a very slight difference between the casks and the bottles. The total loss of chlorine in all forms (correcting that found in the casks as in column *b*) amounted to:—

	In the casks.	In the bottles.
A.....	0.50	0.86
B.....	0.67	0.43
C.....	0.65	0.68

It is very remarkable that the small quantity of *chlorate* originally present was found to have completely vanished after four months' keeping: the *chloride* increased during the eleven months in the casks by 2.09, 1.83, 1.65 per cent.; in the bottles by 1.62, 1.54, 1.38 per cent.

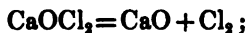
Pattinson remarks that when storing the bleach in less cool places, the loss of chlorine is probably larger than in his experiments, since he found it to be considerably greater during the summer months than in winter.

In comparison with the above, the statements of Boyer and Durand (Journ. Soc. Chem. Ind. 1891, p. 925) on the changes of bleaching-powder present little interest.

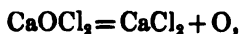
Thümmel (Arch. Pharm. 1884, xxii. p. 20), who examined 15 samples of bleaching-powder taken from druggists' shops, found that they behaved very differently. The average of these samples, some of which were kept in small paper bags, was 31.2 per cent., and even when most carelessly kept in open vessels the bleach showed from 23 to 27 per cent. available chlorine.

The changes taking place in *solutions* of bleaching-powder when kept under varying conditions have been described, p. 438. The transformation of the same into *chlorate* will be mentioned in Chapter XXII.

According to Opl (Dingl. Journ. ccxv. p. 237), bleach yields, when decomposed by heat alone in the absence of moisture,



i. e. chlorine is evolved; but in the presence of moisture (which in practice is always present), bleach both in the solid state and in solution decomposes thus:—



but always with simultaneous formation of chlorate, as has long been known [according to the equation



(Our experiments, quoted p. 424, agree with Opl's so far as the action of moist air is concerned, but prove that even in dry air not only CaO and Cl, but also CaCl<sub>2</sub>, O, and CaCl<sub>2</sub>O<sub>6</sub> are formed.) The action of light could not be distinguished from that of heat; only in direct sunlight chlorous acid was formed. When bleach decomposes spontaneously under ordinary circumstances, chiefly oxygen is evolved, but little chlorine, and some calcium chlorate. Such a decomposition is caused principally by the bleach spontaneously heating, owing to a mutual reaction of its constituents—not while lying in the chamber, but on being mixed and taken out, as Opl proved by many experiments; this is caused by the fact that in the formation of bleach a migration of the water takes place, and the middle layer becomes poorest in water; on mixing the different layers (comp. p. 472) the compounds CaOCl<sub>2</sub> and CaCl<sub>2</sub> are hydrated with evolution of heat; so that the temperature of bleach in the casks may rise to 37½° or even 44° C., which quite suffices for explaining its "spontaneous" decomposition, as this commences at 37½°. The formation of calcium chlorate can only occasion a slight evolution of heat. Hence Opl recommends conveying the chlorine-gas well cooled into the chambers, employing the lime with as much water as practicable, never allowing the chambers to get warmer than 25°, keeping them very clean, so that no bleach remains in them, and never packing the finished bleach directly into casks, but mixing it well and leaving it in shallow wooden boxes with lids to cool at least to 21° C., turning it over several times before it is packed.

#### *Yields and Costs.*

The *yield of bleaching-powder* from slaked lime ordinarily amounts to once and a half the weight of the latter; but with very good work 166 parts of strongest bleach are obtained from 100 parts of lime as charged. For making a ton of 35-per-cent. bleach very different quantities of manganese are required, depending upon its quality, the way in which the process is carried out, and the tightness of the apparatus. Theoretically bleach of 35 per cent. in the cask, or 36 per cent. in the chamber, only requires 44 per cent. MnO<sub>2</sub>; i. e. 100 parts require 73·5 parts of 60-per-cent. manganese, or 63 parts of 70-per cent. manganese. But it is considered very good work

if only 90 parts of the former, or 75 parts of the latter are used; and the average may be taken as 100 parts of 60-per-cent., or 90 parts of 70-per-cent. manganese ore to 100 parts of 35-per-cent. bleach. In Wright's experiments (Chem. News, xvi. p. 126) the loss of chlorine was about 25 per cent. of that calculated from the manganese. The loss is mostly caused by incompletely dissolving the latter: the chlorine escaping will rarely exceed 5 per cent.; otherwise its smell would be intolerable.

In many works the hydrochloric acid is not measured, and its quantity varies even more than that of the manganese ore; because, apart from the causes of loss noticed there, it depends also upon the quality of the manganese and the way of treating it. Theoretically, 100 parts of 36-per-cent. bleach require 74 parts dry HCl, or about 250 hydrochloric acid of 32° Tw. Practically, rarely less than 400 to 450 parts are used, and relatively even more with weak acid. The French factories, employing small stoneware stills and strong acid, are said to work most advantageously as to hydrochloric acid. In England, when native manganese ore is employed, 600 to 700 acid of 28° Tw. are reckoned, upon 100 strongest (39-per-cent.) bleach. In France (according to Payen's 'Précis,' 1877, i. p. 553) 100 parts of hydrochloric acid of 36° Tw. are said to yield 35 parts of bleach of 110 French degrees=35 per cent. chlorine; but in summer only bleach of 100 degrees=31½ per cent. chlorine can be made. Favre (Monit. Scient. 1876, p. 276) states that 1000 kilog. of bleach of 110 degrees require only 2220 kilog. acid of 36° Tw.; but this is incredible.

The *cost* of making 100 kilog. of bleaching-powder 100° G.L. (=32 per cent. chlorine) by the old process at a Continental works in 1875, as taken from the books, was:—

	Kilog.	At frs.	Frs.
Hydrochloric acid 20° B.....	475	15·50	7·37
Manganese ore .....	94·3	138·00	13·02
Lime .....	57·4	35·54	2·04
Coals .....	82·7	14·00	1·16
Wages .....	.....	.....	2·23
Repairs .....	.....	.....	1·20
General expenses .....	.....	.....	0·50

No casks are mentioned.

27·52

The costs for manufacturing bleaching-powder by the Weldon and Deacon processes have been given, pp. 366 and 414.

## CHAPTER XXI.

## BLEACH-LIQUORS.

*Liquid Chloride of Lime.*

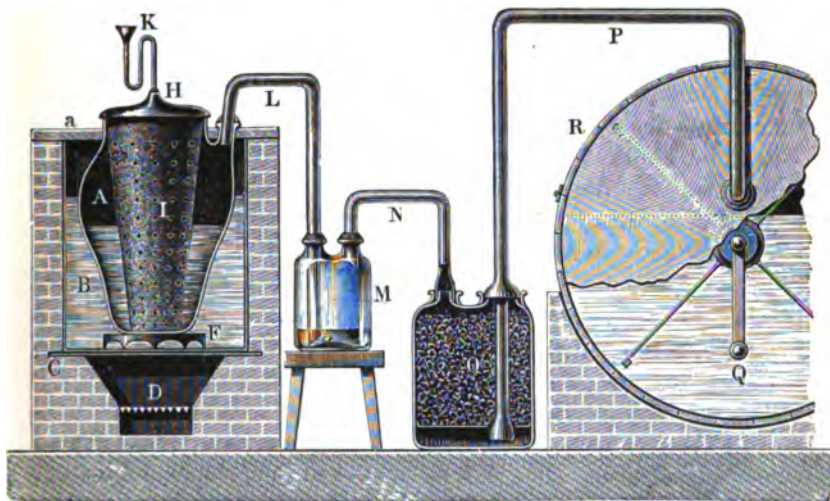
DRY bleaching-powder will probably always remain that form in which the bleaching-properties of gaseous chlorine are fixed most easily and cheaply and made fit for carriage. But this advantage cannot be secured without the drawback that about one third of the lime is not converted into the bleaching-compound  $\text{CaOCl}_2$ . Further, bleaching-powder must be dissolved and settled before use, which is not an easy task. If, therefore, a manufacturer wishes to prepare a bleaching-compound for his own use, it is undoubtedly much better to absorb the chlorine in *milk of lime*, as in liquid bleach no excess of lime is required, and a mixture of calcium hypochlorite and chloride can be directly obtained. In this way the bleachers of Lancashire, Alsace, &c. regularly used to make their own bleach-liquor. Nowadays they do this only exceptionally; but the manufacture of *liquid chloride of lime* (*bleach-liquor*) is still a considerable industry at chemical works situated near bleach-works, where the expense of carriage is not very considerable and casks or carboys can be returned. In South Lancashire, where these conditions exist, much bleach-liquor is made—*e. g.* 5871 tons in 1866. In the North of France bleach-liquor is sent out in canal boats, made of iron and lined with a mixture of tar, pitch, and wax, constructed exactly like those for sulphuric acid, described in Vol. I. p. 746.

Since it is scarcely possible to construct chlorine-stills so as to sustain any considerable pressure, the chlorine in making bleach-liquor can only come into contact with the surface of the milk of



lime; but care must be taken to renew this surface continually by agitation. This is done, for instance, in Pattinson's apparatus (fig. 162). A is the chlorine-still, made of stoneware, standing on the saucer F, in the calcium-chloride bath B; this rests on the

Fig. 162.



metal plate C, and is heated by the fire in D. I is the manganese-funnel, with its cover H and the acid-pipe K (comp. figs. 108 to 111, pp. 301 & 302). The chlorine passes through L into the glass wash-bottle M, partly filled with acid, from this through N into the lead vessel O, filled with lumps of manganese ore, and from this through P into the absorbing-vessel R. This is a horizontally placed wooden cask, lined with lead and provided with the wooden agitating-shaft Q, to which perforated gutta-percha plates are attached. The gudgeons of the shaft are made of teak-wood, the bearings of ebonite. The cask is filled with milk of lime; the chlorine enters above it, but is driven into it by the agitators and is quickly absorbed. The temperature is thereby raised; and the operation must be interrupted before all the lime is dissolved, because otherwise calcium chlorate will be formed. The gas issuing from the cask, especially in the last period, is washed with water, to absorb the chlorine, before it escapes into the air. This apparatus is

evidently only adapted for small factories. If lead pipes are employed, and if these are allowed to dip into the liquid, they are quickly acted upon, chlorine being lost, and oxygen being given off.

Where bleach-liquor is made on a large scale, the same apparatus can be employed as will be described in the chapter treating of chlorate of potash—that is, ordinary chlorine-stills and a connected series of upright cast-iron cylinders with vertical agitating-shafts, for saturating the milk of lime. The work at first is carried on just as for chlorate. The cylinders are charged with about 1 to  $1\frac{1}{2}$  lb. of slaked lime per gallon of water. Care must be taken lest the chlorine be evolved too fast, which would cause too great a rise of temperature. The rule is, not to exceed  $32^{\circ}\text{C}$ .; in *no case* should  $37^{\circ}\text{C}$ . be exceeded. If the temperature should rise to this point, the gas must be stopped at once till the liquid has cooled down. It is very convenient to surround the absorbers with a jacket, between which and the absorber cold water is kept circulating. In any case the operation must be stopped when the specific gravity of the liquor has risen to 1.040; otherwise it will be changed into a solution of calcium chlorate. This happens sometimes after all: hence it is very convenient to combine the manufacture of chlorate with that of bleach-liquor, because then any such spoiled batches can be worked for the former.

For the manufacture of bleach-liquor the chlorine from the Deacon process is very well adapted, all the more as there is here no necessity for drying it with sulphuric acid. It is, in fact, extensively employed for this purpose, its dilution being harmless in this case.

In France bleach-liquor is manufactured in brick vats of 100 to 140 cubic feet capacity, with a mechanical agitator moved by means of a pulley and belt; during the operation they are closed by covers, made of iron or of wood lined with lead, hinged on one side and movable on the other by means of a pulley, chain, and balance-weight. The joint is luted with clay. The chlorine acts only on the surface of the milk of lime, which is constantly renewed by the agitator. The charge is prepared from 9 cwt. of slaked lime and 3 tons of water. The chlorine is passed in slowly, so that the temperature does not exceed  $30^{\circ}$  or  $35^{\circ}\text{C}$ .; as soon as a test of a sample shows that the available chlorine in the liquor is  $=15^{\circ}$  Gay-Lussac (=not quite 5 per cent. chlorine by weight),

the gas is stopped, the liquor is allowed to rest a little and is run into settlers made of bricks set in cement. A good deal of unused lime remains in the vats.

The following, very convenient, apparatus is employed in the North of France :—Four large, horizontal wrought-iron cylinders are placed in tiers on an inclined plane. All of them are provided with agitating-shafts, to which buckets are attached which constantly bring the lime up from the bottom. Both the milk of lime and the chlorine gas enter first into the top cylinder and gradually pass through all the others ; from the fourth and lowest cylinder the bleach-liquor issues with a strength of 18° to 20° Gay-Lussac (6 to 7½ per cent. available chlorine) and upwards. This process goes on continuously, and requires only one man for superintendence and two for preparing the milk of lime. The gas is drawn away from the bottom cylinder by a Körting's injector, so that there is an inward suction of about ½ inch water in the cylinders.

An improvement in the manufacture of bleach-liquor was proposed by Deacon (pat. No. 3309, 1872). The slaked lime is to be replaced by calcium carbonate, in which case the reaction is



*i. e.* free hypochlorous acid is formed. This bleach-liquor may be employed directly, or converted into the ordinary kind by adding lime, which combines with the hypochlorous acid. Deacon proposed to employ the mixture of hydrated and carbonated lime which remains behind in causticizing soda ; it is to be suspended in water and treated with chlorine, like ordinary milk of lime. Or limestone or chalk in lumps may be employed, charged into a tower made of suitable material and always kept moist by water or weak bleach-liquor. This kind of operation is especially recommended for chlorine gas diluted with CO<sub>2</sub> or otherwise, *e. g.* that made by Deacon's own process ; but it has not been introduced in practice, which will be easily understood since under these conditions most of the hypochlorous acid must pass into chlorate (pp. 420 and 487).

According to Solvay (pat. No. 171, 1877) the calcium and magnesium silicates or aluminates, obtained by his patented process No. 77, 1877, are moistened, treated with chlorine, converted into hypochlorites, and then separated from the liberated silica and alumina by dissolving.

Analyses of bleach-liquor always show a slight excess of free lime, without which the transformation of the hypochlorite into chlorate could not be prevented. Thus Davis (Chem. News, xxvii. p. 225) gives the following analysis of bleach-liquor:—

CaOCl <sub>2</sub> .....	13.52
CaCl <sub>2</sub> in excess.....	1.17
CaO .....	0.39
Manganese .....	trace
Water (by difference) ...	84.92
	<hr/>
	100.00

The analysis of bleach-liquor is performed in the way described, pp. 429 & 439. Its percentage of bleaching (available) chlorine can be *approximately* found by the table of specific gravities, p. 439.

#### *Chloride of Potash and Soda.*

These bleach-liquors were known even before the discovery of chloride of lime. First *chloride of potash* was manufactured in 1792 at the chemical works at Javel, which is now a suburb of Paris. Hence its name, Eau de Javel, which was later on applied as well to chloride of soda, first prepared in 1820 by Labarraque; the latter has almost entirely supplanted the original Eau de Javel. This is made by passing chlorine gas in the cold into a solution of 1 part of potash (K<sub>2</sub>CO<sub>3</sub>) in 8 parts of water till the liquid begins to effervesce (comp. chloride of soda). Potassium chloride is separated in small crystals, together with silica (from the impurities contained in commercial potash). Since at first it was common to obtain the chloride coloured pink by the accidental presence of some salt of manganese, the consumers got accustomed to it, and this colour afterwards had to be artificially produced by adding a little still-liquor.

A very active dry bleaching compound is made by passing chlorine through a solution of 24 parts potash with 1 part water, when a mixture of potassium chloride, hypochlorite, and carbonate is formed.

*Chloride of Soda (Hypochlorite of Soda).*

This liquor, formerly called Eau de Labarraque, but afterwards mostly Eau de Javel, is made according to two different prescriptions, which yield very different results. According to the first, chlorine is passed into a solution of sodium carbonate. The original prescription, given in 1820 by Labarraque (*Journ. Chim. méd.* ii. p. 165), was:—Chlorine, made from 576 parts salt, 576 sulphuric acid, 448 water, and 448 manganese, is passed into a solution of 2500 parts crystallized sodium carbonate in 10,000 water. At present this liquor is made by passing chlorine into a solution of sodium carbonate in at least 10 parts of water till the liquid begins to effervesce or till it bleaches litmus. It then contains free hypochlorous acid along with sodium chloride and bicarbonate:



If further chlorine be admitted, the bicarbonate is also decomposed with effervescence,  $\text{CO}_2$  being liberated and only  $\text{NaCl}$  remaining along with hypochlorous acid:



At the same time also some chlorate is formed, especially if the specific gravity of the liquid rises above 1.06; but this ought to be avoided.

Mayer and Schindler (*Repertor. f. Pharmacie*, xxxi. p. 1) obtain the compound in a solid state by passing the chlorine given off from 10 parts  $\text{NaCl}$ , 8 manganese, and 14 sulphuric acid into 19 parts of dry powdered sodium carbonate, moistened with only 1 part of water. The chlorine is slowly absorbed with evolution of heat. The product is a white powder possessing a peculiar faint smell, and is soluble in 8 parts of water.

To the same class of bleach-liquors belongs that which is obtained by passing chlorine into caustic-soda solution, under such precautions as are adapted for avoiding the formation of chlorate, that is at a moderate temperature and in such manner that there is always a little undecomposed alkali present. The reaction is then simply:



Such bleach-liquor is made especially in the North of France,

testing 22°, 33°, and 49° Gay-Lussac (=6·3, 9·5, and 15·5 per cent. available chlorine).

The second kind of liquor is made from bleaching-powder and carbonate or sulphate of soda. If to a clear solution of bleaching-powder sodium carbonate be added, calcium carbonate is precipitated and the solution contains sodium hypochlorite and chloride. In the place of sodium carbonate, sulphate or, preferably, bicarbonate may be employed. This liquor is perfectly analogous to a solution of bleaching-powder, and quite different from that obtained by passing chlorine into soda; whilst the latter dissolves ferric hydroxide, and consequently takes away ink-spots, the liquor made from bleaching-powder turns the ink-spots iron-rust-coloured. The latter liquor is best prepared with sodium bicarbonate, because the precipitate settles much better than with monocarbonate. In the former case a crystalline, in the latter a pasty precipitate is formed. A slight excess of bicarbonate in the liquid is very useful for many purposes. Such a liquor is stated to bleach copper engravings in a minute without any damage to the paper, especially if the latter be at once dipped into a weak solution of sodium bisulphate (? *Chem. News*, xi. p. 132). A very cheap process, yielding a liquor that keeps well, is the following—passing chlorine into a mixture of milk of lime and sulphate of soda. This is the plan followed at Malétra's works at Rouen. The pharmaceutical preparation (*liquor natri hypochlorosi*) is obtained by shaking 20 parts bleaching-powder with 100 water, adding a solution of 25 parts soda crystals in 50 water, settling, and decanting. 1000 parts of this liquid ought to contain at least 5 parts of available chlorine.

This very old preparation of bleach-liquor was again patented in France by Coutelle in 1873 (decomposing a solution of bleaching-powder by sodium carbonate or sulphate). He sold his liquor as "*extrait d'eau de Javel*," with 30° to 40° Gay-Lussac (9½ to 13 per cent. chlorine), with the assertion that such liquor was "neutral" and kept much better than that prepared by the action of chlorine on caustic soda, which always contains some free alkali. This assertion is wrong in a twofold sense. Firstly, the liquor does not become less stable by the presence of free alkali (this is only the case if free  $\text{CO}_2$  or  $\text{NaHCO}_3$  is present); secondly, the liquor made from bleaching-powder must always contain a little free alkali, as the solution of bleaching-powder

always contains some free lime (comp. p. 486). These solutions of sodium hypochlorite, also called "esprit de Javel," are much used in France (Lequin, Official French Report, Paris Exhibition, 1889, p. 88).

Herison and Lefort (Monit. de Teint. 1891, p. 309) once more recommend a bleach-liquor made from equal parts bleaching-powder and sulphate of soda, as something new and specially excellent.

Young (Engl. pat. 653, 1882) asserts that it is possible to prepare a very superior bleach-liquor as follows:—A solution of bleaching-powder is decomposed by sodium, potassium, or magnesium sulphate, and sodium carbonate is added until all the lime has been precipitated. [This is without doubt, if sodium or potassium sulphate is used, exactly the same as a solution of sodium hypochlorite made directly by adding  $\text{Na}_2\text{CO}_3$  to bleaching-powder solution. If magnesium sulphate is used, most of the magnesia would also be precipitated by the sodium carbonate.]

The following analyses refer to various samples of sodium hypochlorite occurring in the French trade—A from the Paris market; B from Malétra's works at Rouen; C from Bruges (the latter partly decomposed); B and C contain much caustic soda:—

	A.	B.	C.
Degrees Baumé at 15°.....	21	32·2	29·6
Chlorometric degrees (Gay-Lussac)...	29·2	47·05	32·0
Available chlorine.....grams per litre	92·78	149·5	101·7
Chlorine as chloride.....	—	28·0	—
Chlorine as chlorate ...	—	trace	—
Total chlorine .....	101·50	177·5	169·68
Sulphuric acid (as sulphates) ..	16·82	—	—
Total soda .....	—	266·7	192·0

C. A. Martin (Dingl. Journ. ccxlv. p. 46) describes an "inodorous bleach-liquor" of peculiar composition. The following solutions are added to a solution of bleaching-powder:—(1) 500 grams potassium nitrate, dissolved in 10 litres of a 5-per-cent. solution of aluminium sulphate; (2) 100 grams salicylic acid, dissolved in 1 litre spirit of wine; (3) 500 grams potassium nitrate and 500 grams sodium sulphate, dissolved in 5 litres of water. This is supposed to increase the bleaching action and to avoid the ordinary smell of chlorine-bleached fabrics [?].

Barnett and Slade (pat. Oct. 3, 1872) add to a solution of bleaching-powder sufficient solution of sodium carbonate to precipitate all the lime as carbonate, and pass carbonic acid into the decanted clear solution till all the bases are converted into bicarbonates. Thus a very efficient and yet mild bleaching and disinfecting agent is obtained.

The ordinary chloride of soda is a colourless or faint-yellow liquid, smelling like bleaching-powder and having an astringent taste. Upon vegetable colouring-matters it shows first the reaction of an alkali, and then bleaches them. On evaporation *in vacuo* needle-shaped crystals are said to be obtained, which on being redissolved in water reproduce the original bleach-liquor; but when this is evaporated in the air, oxygen escapes and potassium chloride and a little chlorate remain behind. Acids evolve from it carbonic acid and chlorine; in the air, also, it decomposes and soda crystals are deposited.

Chloride of soda is preferred to chloride of lime in the bleaching of linen and for several other purposes.

#### *Chlorozone.*

An English patent, by Count Dienheim-Brochocki (No. 4483, 1876), describes the following bleaching-compounds. He passes cooled and dried chlorine through a solution of caustic soda or potash cooled down to 10° C., and in 24 hours obtains a crystalline product possessing extremely strong bleaching properties. By evaporating the mother liquor in a vacuum more crystals are obtained. Or chlorine is passed over a thin layer of an alkaline carbonate spread over the cooled shelves of a close apparatus; the issuing gas is passed through a very strong solution of caustic alkali. The hypochlorite obtained here is mixed with the partially saturated carbonate of the first apparatus; by this the hypochlorite is solidified, as the carbonate attracts its water of solution. In the place of that carbonate other substances having a strong affinity for water may be employed. The product is said to preserve its bleaching-properties longer than any liquid hypochlorite. It may be prepared in a granulated form by stirring the solution just before solidifying, or in the form of cakes by pouring it into a mould and causing it to solidify by the application of ice. The product is easily packed, as in the solid state it acts neither on metals nor on organic substances. This product has the advantage



of being completely soluble in water, and acting very uniformly on the fibre without injuring it; its economy is more doubtful. It consists of 80 per cent. soda crystals, 8.5 NaCl, and 11.5 sodium hypochlorite. The commercial product (also known as "chlorozone" or as "essence de Boulogne") is crystalline, resembling soda, smells of chlorine, dissolves in water without residue, and is very hygroscopic: the great durability claimed by the inventor does not exist; for a sample which was kept for some time in a stoppered bottle showed only 1.33 per cent. bleaching chlorine.

A second patent of the same inventor's (No. 2349, 1878) swarms with absurd assertions, accompanied by reaction-equations with unequal sides. "Chlorozone," incomparably better than chlorine, bleaching-powder, or hypochlorite of soda, is now to be prepared by passing into a solution of caustic alkali a mixture of atmospheric air and hypochlorous acid, made by treating bleaching-powder with mineral acids, in which case the first liberated chlorine is at once oxidized by atmospheric air to hypochlorous acid (!). If this is allowed to act on caustic soda in such manner that the "hypochlorous acid" remains in excess, "acid chlorozone" is formed, that is, a solution of sodium chlorate and free hypochlorous acid; otherwise "alkaline chlorozone," containing sodium chlorite, hypochlorite, and chloride is obtained. Thus the atmospheric oxygen can be made to double or even treble the bleaching-power of chlorine by the action of chlorate, &c.!

In a further patent (Germ. pat. 34016) Count Dienheim-Brochocki states that chlorine, made from manganese peroxide with hydrochloric acid &c., is nothing like so good and cheap as that liberated from bleaching-powder by dilute acids. The hypochlorous acid, first liberated in the second state, splits up to a great extent into chlorine and oxygen. The mixed gases are passed through a solution of sodium sulphate or calcium chloride, then through powdered manganese ore, and are then submitted to the influence of the electric current, which causes the oxygen to be quickly ozonized and to combine again with the chlorine. The chlorine oxides thus formed are passed into a concentrated caustic-soda solution and yield a product of great bleaching-power. Instead of the electric treatment, two separated gaseous currents may be employed, viz. one of ordinary chlorine and another of ozonized oxygen.

These bleaching-compounds were energetically "puffed" by French and English pamphlets, articles in professional journals and newspaper advertisements, and, unfortunately, even men of undoubted scientific standing were induced to support this puffing, although with a certain reserve. This naturally led to an extensive sale to consumers. But the absolute nonsense, both of the theoretical views and of the alleged practical results obtained with chlorozone, was soon proved from two independent sources. Lunge and Landolt (Chem. Ind. 1885, p. 337) showed that "chlorozone," made exactly according to prescription, is nothing but a solution of free hypochlorous acid in a solution of NaCl, with small quantities of free chlorine and  $\text{NaClO}_3$ , but without a trace of chlorous acid or chlorine peroxide. Another sample, prepared *without the current of air*, proved to be identical with the former, as might have been expected. In the same way analyses of the distillate from bleaching-powder and sulphuric acid showed no difference, whether air was passed through or not.

Soon after Storch (Ber. österr. Ges. f. Förd. d. chem. Ind. 1885, p. 102) published an investigation, made with an original sample of commercial chlorozone, evidently the "alkaline" variety, whereas that prepared by myself and Landolt was "acid" chlorozone. Storch found sodium hypochlorite, chloride, and free hydrate, a little more of the latter than in ordinary Eau de Javel. The bleaching-action was slower than that of the latter; the results were identical when much free alkali was added to Eau de Javel.

Since these papers were published the advertisements respecting "chlorozone" have disappeared from the columns of professional journals.

Osterberger and Capelle (Monit. Scient. 1890, p. 1137) have analyzed two samples of commercial "chlorozone" (A, B) and of "chlorogen" (C), as follows:—

	A.	B.	C.
Degrees Baumé.....	24	15.5	21.1
„ Gay-Lussac .....	36.4	33.8	29.8
Available chlorine, grams per litre	117.68	107.40	94.70
Inactive chlorine „ „	29.96	16.20	24.99
Sodium carbonate „ „	17.34	37.85	38.94
Sodium hydrate „ „	19.58	4.08	4.90

This once more proves that those articles are nothing but ordinary solutions of "chloride of soda," which always contain some free alkali to make them fitter for carriage, and that all assertions going beyond this are simply deceptions practised on the consumers.

*Magnesia Bleach-liquor.*

This can be made by decomposing a solution of bleaching-powder with Epsom salts and decanting from the gypsum formed. It has been proposed for bleaching by Claussen, and again by Ramsay; it is said to bleach more rapidly, and not to turn straw, flax, hemp, &c. brown, as it is free from lime; but it suffers decomposition more quickly than chloride of lime. The separated magnesia does not at all injure the fabrics (Bolley and Jokisch, Schweiz. polyt. Zeitschr. 1866, p. 120). Such a liquor was patented by Oliver, Grantham, Sinnock, and Leverson (No. 2351, 1861), without adding anything new. F. Hodges has shown that a liquor of the same kind (prepared from ordinary bleaching-powder and kieserite) can bleach linen fabrics without exposure on grass, if they have previously been steeped in a hot solution of sodium carbonate.

Balard prepared a bleaching-liquor by dissolving magnesia in aqueous hypochlorous acid; Grouvelle by passing chlorine into magnesia suspended in water.

None of these solutions had been more closely investigated until Lunge and Landolt (Chem. Ind. 1855, p. 340) undertook this task. They tried first to prepare a bleaching-magnesia, analogous to bleaching-powder, by treating solid magnesium hydroxide with chlorine, either in the dry or in the moist state; but they did not obtain anything fit for use, viz. a mass with only 0.15 available and 4.8 chloride-chlorine.

Now chlorine was passed into a milk of magnesium hydroxide and water, at temperatures between 0° and 100°. Even at 0°, together with magnesium hypochlorite, much chlorate was formed, more than corresponding to half of the chlorine entering into the reaction. At 15° a little more chlorate was formed, together with much hypochlorate, some of which was changed into chloride, with evolution of oxygen. In both solutions the hypochlorite is easily converted into chlorate, not merely by heating to 50°, but even by prolonged agitation by a current of air at ordinary temperatures. At 70° C. from the first mostly chlorate was formed,

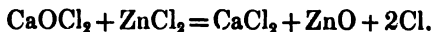
with a little chloride, produced by loss of oxygen. Hence magnesium hypochlorite *in statu nascendi* does not possess much stability and is easily transformed into chlorate.

Very different from this is the behaviour of a product obtained by decomposing a solution of bleaching-powder with magnesium sulphate. Here no conversion of hypochlorite into chlorate occurs, a very slight production of  $MgCl_2$  by loss of oxygen is observed, but no splitting off of free  $HOCl$ .

The stability of this bleaching-solution is almost equal to that of bleaching-powder solutions. Kept in closed vessels in the dark, it had lost only  $\frac{1}{60}$  of its available chlorine after keeping for 33 days; kept open in the dark, no change was observed after 6 days, and after 33 days a loss of not quite  $\frac{1}{2}$  of bleaching-powder. Kept in closed bottles in diffused daylight, the stability of this solution was superior to that of all other bleach-liquors; after 33 days  $\frac{9}{10}$  of the available chlorine was still present. This is therefore a very good bleaching-solution, if kept from the light.

#### *Zinc Bleach-liquor.*

If a solution of zinc sulphate be added to a solution of bleaching-powder, calcium sulphate is precipitated, and the zinc hypochlorite formed at once splits up into zinc oxide and a solution of free hypochlorous acid. Zinc chloride acts similarly; for a saturated solution of zinc in strong hydrochloric acid decomposes as much bleaching-powder as half its weight of concentrated oil of vitriol (Varrentrapp). The reaction must be



Accordingly these zinc salts can be employed for liberating chlorine from bleaching-powder without the use (often objectionable) of strong acids, and thus bleaching very quickly. When this mixture is employed in bleaching paper-pulp, the precipitated calcium sulphate and zinc oxide remain in the pulp. This solution was introduced by Sacc (Wagner's *Jahresb.* 1859, p. 548), and has been recommended by Varrentrapp (*ib.* 1860, p. 189).

Balard also treated zinc oxide with a solution of hypochlorous acid, but obtained only a very unstable product; Grouvelle treated

zinc oxide with water and chlorine and equally obtained only a very unstable solution. Neither makes any mention of chlorate.

Lunge and Landolt (Chem. Ind. 1885, p. 341) have investigated these solutions more closely. No solid bleaching-compound can be obtained with them, no more than with magnesia (p. 493). When treating zinc oxide, suspended in water, with chlorine at 15° C. much chlorate is formed, together with hypochlorite, but not quite so much as in the case of magnesia. On heating this liquid, or on passing in the chlorine at a higher temperature, the formation of chlorate is much larger, but in the presence of an excess of zinc oxide a considerable quantity of hypochlorite is produced, even at 70° and 100° C. While, therefore, zinc hypochlorite resists the transformation into chlorate somewhat better than the magnesium salt, it has a greater tendency, in the absence of an excess of zinc hydroxide, to split up into chloride and oxygen.

This is confirmed by the behaviour of the bleach-liquor obtained by adding a solution of  $\text{ZnSO}_4$  to one of bleaching-powder. Here no smooth double decomposition takes place, but the available chlorine decreases, part of the zinc hypochlorite at once splitting up into  $\text{ZnCl}_2$  and free oxygen. There is also some formation of free  $\text{HOCl}$  with precipitation of zinc oxide or oxychloride.

The zinc bleach-liquor is less stable than those previously described. Even when kept in closed bottles in the dark it begins to lose strength from the first day, and on the 15th day  $\frac{1}{4}$  of the bleaching-chlorine has disappeared. The further decrease is slower, and even on the 33rd day not much greater. The liquor when kept open in the dark gradually lost its bleaching-power during the whole period, about  $\frac{1}{4}$  of it being left on the 33rd day. On keeping it in closed bottles in diffused daylight the decrease of bleaching-power was quite steady and much stronger, so that on the 33rd day only  $\frac{1}{4}$  remained.

#### *Alumina Bleach-liquor.*

Orioli (Wagner's Jahresb. 1860, p. 188) recommended, especially for paper-mills, a bleach-liquor made by decomposing equivalent quantities of a solution of bleaching-powder and aluminium sulphate; this had been known for many years as Wilson's bleach-liquor. Gypsum is thrown down, and aluminium hypochlorite

remains dissolved. This is very unstable, and hence can be employed for bleaching without adding an acid, splitting up into aluminium chloride and active oxygen. Consequently the liquid always remains neutral, and the difficulty caused by the obstinate retention of free acid in the fibre, by which it is strongly acted upon on drying, in this case does not exist. The aluminium chloride also acts as an antiseptic, so that the paper stock can be kept for many months without any fermentation or other decomposition. The solution is allowed to act for ten minutes in the rag-beating engine. In the case of fabrics, yarns, &c. a solution of 4 parts aluminium hypochlorite in 200 water is employed, and the stuff left in it for two or three hours. This solution can also be employed for preserving animal substances, embalming, &c., as the aluminium chloride forms very stable compounds with the albuminoid and colloid bodies and destroys the germs of putrefaction. Lastly, it is also applicable as a mordant in dyeing in lieu of aluminium acetate, as the hypochlorous acid readily escapes and the alumina remains combined with the fibre.

Grouvelle stated that aluminium hydrate, suspended in water, is not dissolved by chlorine. Lunge and Landolt (Chem. Ind. 1885, p. 342) confirm this; their experiments show the improbability of even a merely temporary formation of aluminium hypochlorite taking place. Nevertheless this compound exists in the solution prepared according to Orioli's instructions, which they examined more closely. They found that here, as in the case of zinc, some free hypochlorous acid is split off at once, which accounts for the great bleaching-power of these solutions and their want of stability. The solution kept very well when preserved in closed vessels in the dark, like the hypochlorites of calcium and magnesium (contrary to the behaviour of the zinc compound); but when kept in the dark in open vessels it lost half of its bleaching-power within 33 days, that is exactly as much as the zinc solution, and no doubt from a precisely similar cause, viz., through the evaporation of free hydrochlorous acid, which constantly forms again. On keeping in closed bottles in diffused daylight it lost  $\frac{2}{3}$  of its bleaching-power within 33 days, again just the same as the zinc (and the bleaching-powder) solution.

R. Weiss (Germ. pat. 38048) prepares bleach-liquor by passing chlorine into a solution of sodium aluminate, or into calcium or magnesium aluminate suspended in water.

The presence of free hypochlorous acid in the solutions of zinc and aluminium hypochlorite, which is *not* found in the solutions of calcium and magnesium hypochlorite, was also very clearly proved by the bleaching-tests made by Lunge and Landolt (*loc. cit.* p. 345). They submitted cloth, dyed with Turkey-red, to the various solutions, under the same conditions and at the same chlorometric degree. The red colour was found discharged in solution of chloride of lime after 48 hours, in magnesia bleach-liquor after 36 hours, in zinc bleach-liquor after  $1\frac{1}{2}$  hours, in alumina bleach-liquor after  $3\frac{1}{4}$  hours. The same speed of bleaching could be attained in the first two liquors by means of carbonic acid or dilute acetic acid, which set some HOCl free.

## CHAPTER XXII.

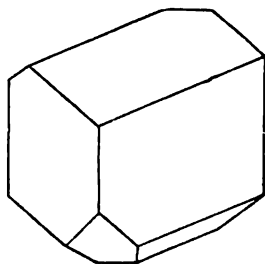
## THE CHLORATES.

## CHLORATE OF POTASH.

POTASSIUM chlorate, according to Kopp's *Gesch. der Chemie*, iii. p. 362, seems to have been prepared already in the 17th century, as is proved by two passages in Glauber's writings; but its nature was not recognized, Glauber taking it for saltpetre. Its real discovery and investigation are due to Berthollet, 1786-88. Gay-Lussac, Graham, and others gave prescriptions for its preparation; but only that of Liebig made its manufacture on a large scale economically possible. Since then this salt has entered into the cycle of alkali-making, because its manufacture, like that of bleaching-powder, formerly, before the development of electrolysis, was only possible in connexion with the preparation of saltcake from common salt and sulphuric acid. Certainly much fewer works make chlorate than bleach; the former belongs to the finer chemicals, which as a rule leave a larger margin of profit than articles made in large quantities but which are only saleable to a restricted extent and can only be made with much more trouble and care. It is, for instance, a condition in trade that chlorate of potash should not contain more than 0.05 per cent. chlorine as chlorides, or should consist of 99.9 per cent. chemically pure  $\text{KClO}_3$ .

Potassium chlorate forms transparent brilliant crystals of the monoclinic system (fig. 163). The two prevailing prisms form apparent rhombohedra. Large crystals are rarely found; the salt, as sold, is in small iridescent laminæ and

Fig. 163.





plates. When crystallizing from liquors containing very much calcium chloride (as in the crude crystals made at the factories) it shows an entirely different habit, viz. small, pointed, needle-shaped crystals. This is caused by a different development of certain faces of the crystals without any alteration of the crystallographic character.

It is softer than rock-salt; its specific gravity is 2.326-2.35. It does not change in the air, has a cooling, astringent, and nitre-like taste. In large quantities it acts as a poison, like all potassium salts. Its chemical composition is:—

K.....	39·13 =	31·92 per cent.
Cl.....	35·46 =	28·92 „
3O.....	48 =	39·16 „

$$\text{KClO}_3 = 122.59 \quad 100.00$$

Potassium chlorate, according to Pohl (Liebig's Jahresb. 1851, p. 59), fuses at  $334^{\circ}\text{C}$ . without losing oxygen; but it decomposes at  $352^{\circ}$  with effervescence, more rapidly at red heat, partly splitting up into potassium chloride and oxygen, and partly, unless the heat is too high, into potassium chloride and perchlorate; on further heating the latter also splits up into KCl and O. The oxygen made from potassium chlorate always contains a little chlorine, free or combined. According to Carnelley (Chem. Soc. Journ. 1878, ii. p. 277), its fusing-point is  $359^{\circ}\text{C}$ .; the temperature at which it begins to decompose must be a little higher.

Potassium chlorate is soluble in water, heat being absorbed. According to Gay-Lussac, 100 parts of water dissolve

At 0° 13°32 15°37 24°43 35°02 49°08 74°89 104°78  
3.33 5.60 6.03 8.44 12.05 18.96 35.40 60.24 pts. by weight.

**According to Girardin,**

At	28°	35°	40°	47°	65°
	9·5	12·3	14·4	18 3	29·1 parts by weight.

Consequently its solubility increases, especially above 50°, at a much higher rate than the temperature. The saturated solution boils at 105° (Kremers). Specific gravity of the solution at 19°·5 (experiments by Kremers, calculated by Gerlach) :—

Per cent. $\text{KClO}_3$ ...	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Sp. gr. ....	1.007	1.014	1.020	1.026	1.033	1.039	1.045	1.052	1.059	1.065

2 x 2

In absolute alcohol it is insoluble, in spirit of wine very little soluble, and the less so the stronger the spirit.

The heat of formation of potassium chlorate from its elements is +94.6, but from KCl and O<sub>2</sub> it is -11.0 calories (for sodium chlorate the figures are +85.4 and -12.3 respectively).

The following methods have been indicated for the preparation of chlorate of potash:—

1. That of Gay-Lussac. A solution of one part of potassium hydrate in 3 parts of water is completely saturated with chlorine gas, allowed to stand for a few days, and then heated to ebullition so as to decompose the hypochlorite:



According to Morin (Ann. Chem. Phys. xxxvii. p. 154), only 1 equivalent of potassium chlorate to 18 of chloride is obtained, because on evaporating the solution much oxygen escapes. Instead of caustic potash a solution of potassium carbonate may be saturated with chlorine gas; but this is much more difficult, and causes much loss of chlorine and hypochlorous acid, for which reason caustic potash is preferable. In either case a very large quantity of potassium hydrate or carbonate is converted into the much less valuable chloride, which is also very difficult to separate from chlorate; and hence this process does not possess any technical interest.

2. Graham (Phil. Mag. xviii. p. 518) proposed to save potash by saturating an intimate mixture of 1 equivalent of potassium carbonate and 1 of dry calcium hydrate (*i. e.* 100 K<sub>2</sub>CO<sub>3</sub> + the hydrate from 40 CaO) with chlorine. The absorption takes place quickly, the temperature rising to 100° C. and the water being evaporated. The saturated mass is heated in order to decompose all hypochlorite and extracted with water; potassium chlorate and chloride are dissolved, and calcium carbonate remains behind. This process is also not applicable in industry, compared with Liebig's; neither is this the case with a proposal made by Crace Calvert as late as 1850, for passing chlorine into a heated mixture of caustic-potash liquor and lime (Chem. Soc. Quart. Journ. iii. p. 106).

3. From bleaching-powder. Liebig proposed (Mag. Pharm. xxxv. p. 225) to grind up 10 parts of ordinary bleaching-powder with water, and evaporate to dryness. Thus a mixture of calcium chlorate and chloride is formed, which is dissolved in water, filtered

and mixed with 1 part of potassium chloride, and evaporated to dryness. But in this case there is a considerable loss by evolution of oxygen in evaporating (comp. p. 419).

4. The only technically available process was also indicated by Liebig (Ann. Pharm. xli. p. 307). His prescription is to make 1 molecule of potassium chloride and 3 of quicklime into a thin paste with water, to saturate this with chlorine, filter, and to obtain from the solution, which contains only potassium chlorate and calcium chloride, the former by crystallization. The process now employed on the large scale differs from this only in the potassium chloride being added at a later stage, usually only after completely saturating the lime with chlorine.

5. During the last few years the preparation of chlorate by *electrolysis* has become extremely important. It will be described in Chapter XXIX.

In this place we shall only describe the manufacture of chlorate of potash (and soda) by Liebig's process, which was introduced into England in 1847, and is even now the only one used at all works except those employing electrolysis.\*

#### MANUFACTURE OF CHLORATE OF POTASH BY LIEBIG'S PROCESS.

This manufacture embraces the following operations :—

1. Manufacture of chlorine.
2. Absorption of chlorine by lime.
3. Evaporation of the liquor, after converting the calcium chlorate into potassium chlorate.
4. First crystallization.
5. Utilization of the mother liquor.
6. Recrystallizing (refining) the crude salt.

\* The description given in the following pages is principally founded on my personal observations and experience, as already set forth in the first edition of this book, but of course with full regard to all that has been added in the meantime. A monograph on this subject by K. W. Juriach ('Die Fabrikation von chlorsaurem Kali und anderen Chloraten,' Berlin, 1888) has likewise been consulted, so far as it contains useful information. Most of it consists of an extremely minute description of Messrs. Muspratt's works, with needless details of apparatus and of laboratory and warehouse books. Every note taken from it is here duly acknowledged. I have also made use of Péchiney's article in Frémy's 'Encyclopédie Chimique,' tome v. section i. 2nd part, pp. 189 to 216.

### 1. *Manufacture of Chlorine.*

This is performed exactly as in the manufacture of bleaching-powder, and more especially of bleach-liquor. Dilute Deacon chlorine can be used here with great advantage, because it requires no drying with sulphuric acid, just as in the case of bleach-liquor (p. 484), and because, moreover, a contamination with carbonic acid (p. 410) is of no importance in this case.

### 2. *Preparation of Chlorate of Lime.*

The apparatus in which chlorine gas is made to act upon milk of lime, in order to prepare calcium chlorate, may be of very different shape and consist of different material. In most cases they are constructed in such a way that the chlorine enters under a very slight pressure, and acts only on the surface of the liquid, which, however, is only then sufficient if that surface is constantly renewed. Apparatus constructed for greater pressure, in which the chlorine is to be introduced below the surface of the liquid, must be worked with contrivances for pressure or aspiration which render the work very complicated, and which have nearly everywhere turned out impracticable.

The apparatus for manufacturing calcium chlorate altogether resemble in their principles those in which bleach-liquor is made (p. 483 *et seq.*). The difference between both kinds of operation does not at all lie in the apparatus, nor even in the quantities entering into reaction (it is always  $2\text{Cl}$  for  $1\text{CaO}_2\text{H}_2$ ), but exclusively in the way the process is conducted. If the reaction is to be carried only to the formation of hypochlorite, the temperature must be kept low and no excess of chlorine must ever be present; the contrary conditions are valid for the formation of chlorate, but even here the temperature must not rise too high, and the excess of chlorine is utilized later on.

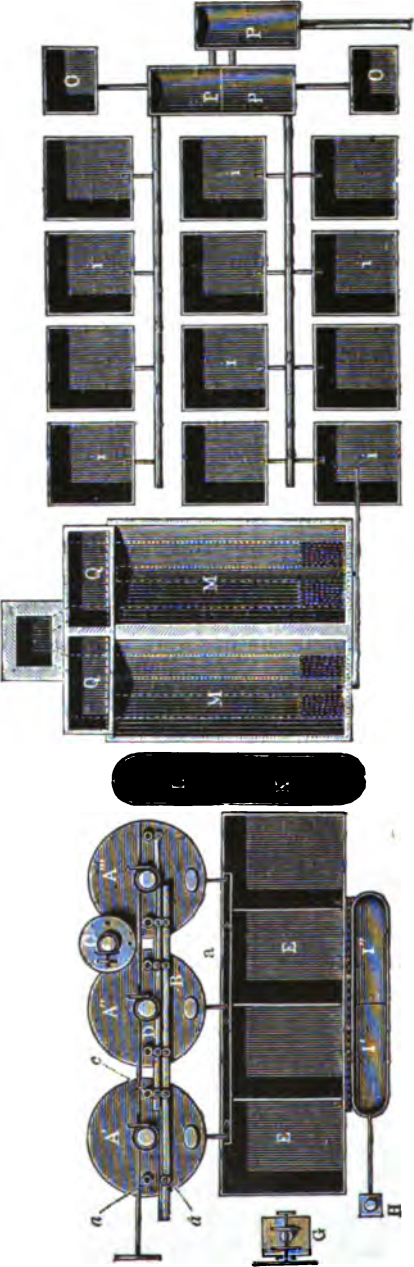
The oldest style of apparatus, long out of use, is described and illustrated in our first edition, vol. iii. p. 295 *et seq.* Jurisch (p. 13 *et seq.*) describes the equally antiquated stone "octagons," which name has been very strangely transferred at some English works to the cast-iron cylinders which have everywhere replaced the former. There is no object served in employing stone, as the presence of lime protects the cast-iron against the action of

chlorine. Jurisch (p. 27 *et seq.*) also gives a minute description of an absorbing vessel, adopted from Kuhlmann's works (Clark's Engl. pat. No. 1181, 1880), in which the chlorine enters just over the bottom of the vessel, and is made to travel upwards in a spiral course by an inverted spout attached to the sides. This plan greatly promotes the absorption. Such apparatus cannot be properly constructed otherwise than of iron lined with lead; at Kuhlmann's works, where it was used for making bleach-liquor, and therefore worked at lower temperatures, it seems to have been very efficient, but even there it has long since been replaced by the apparatus described on p. 485. In the case of calcium chlorate, where the temperature must rise much higher, such leaden apparatus has proved a failure, as can be seen from Jurisch's own statement (p. 30). At all events it involves mechanical aspiration of the chlorine by an exhaustor, working under a pressure of 10 inches of mercury; the effective vacuum in the apparatus still amounted to 4 inches mercurial pressure, or 54 inches water pressure. We need not detain ourselves with a detailed description of this apparatus, as nobody will be tempted to introduce it nowadays.

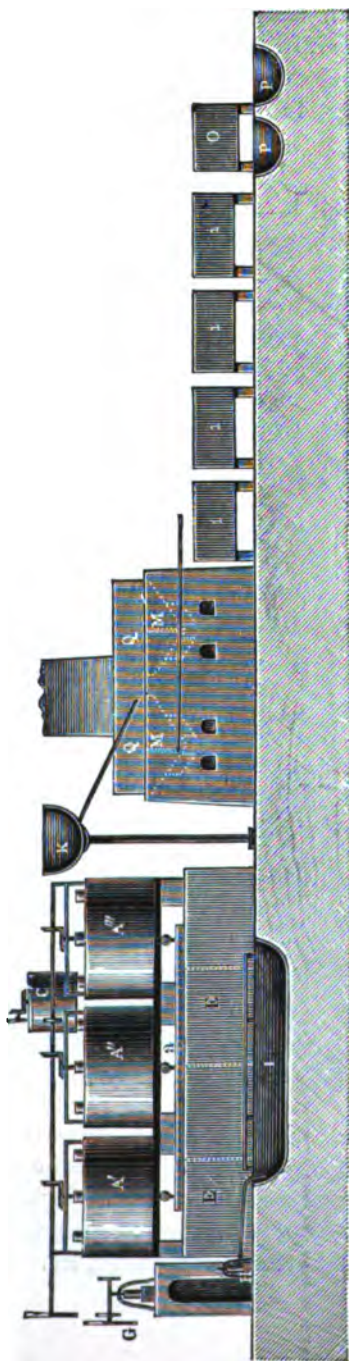
The following is a description of an apparatus employed by myself for the production of chlorate of potash on the large scale. Figs. 164 and 165 show the apparatus for manufacturing the crude salt. The dimensions as given below suffice for making 7 or 8 cwt. of chlorate in 24 hours; but more cylinders may be combined together, and a correspondingly larger production obtained. A' A'' A''' are the absorbing cylinders; B is the main gas-pipe, C the reserve absorber, D the return gas-pipe; E E are the settlers for the calcium chlorate; G is the steam-engine; H a pump for the chlorate liquid from the well I; K a tank for concentrated chlorate liquor, L another for washings; M M boiling-down pans for chlorate liquor; *ii*, crystallizing-vessels for crude salt; O O, drainers for the same; P P, catch-wells for any salt carried away on running-off the mother liquors; Q a pan (heated by the waste heat of the pans M M) for dissolving any crusts and mud of chlorate and running this solution straight into the pans M M.

The *absorbers* A' A'' A''' are made of cast iron, even stone covers have been mostly abandoned. The details of their construction can be seen from fig. 166 (sectional elevation) and fig. 167 (top view). They are 10 feet wide and 5 ft. 6 in. high; the bottom and top are each made in one piece, the shell in segments; all

Fig. 164.

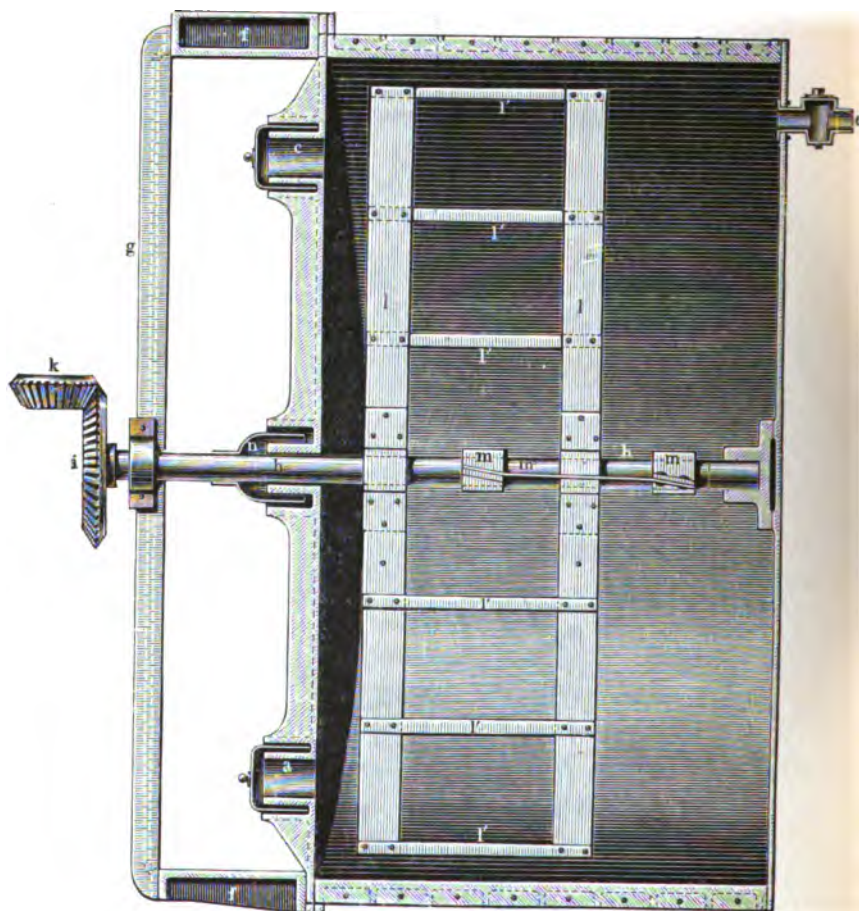


**Fig. 105.**



joints are made with flanges and screwbolts and rust-cement. The metal is only one inch thick ; but the flanges are strengthened in the usual way ; and so is the top by six radial ribs. There are three 6-inch openings in the top (*a*, *b*, *c*), for introducing and

Fig. 106.

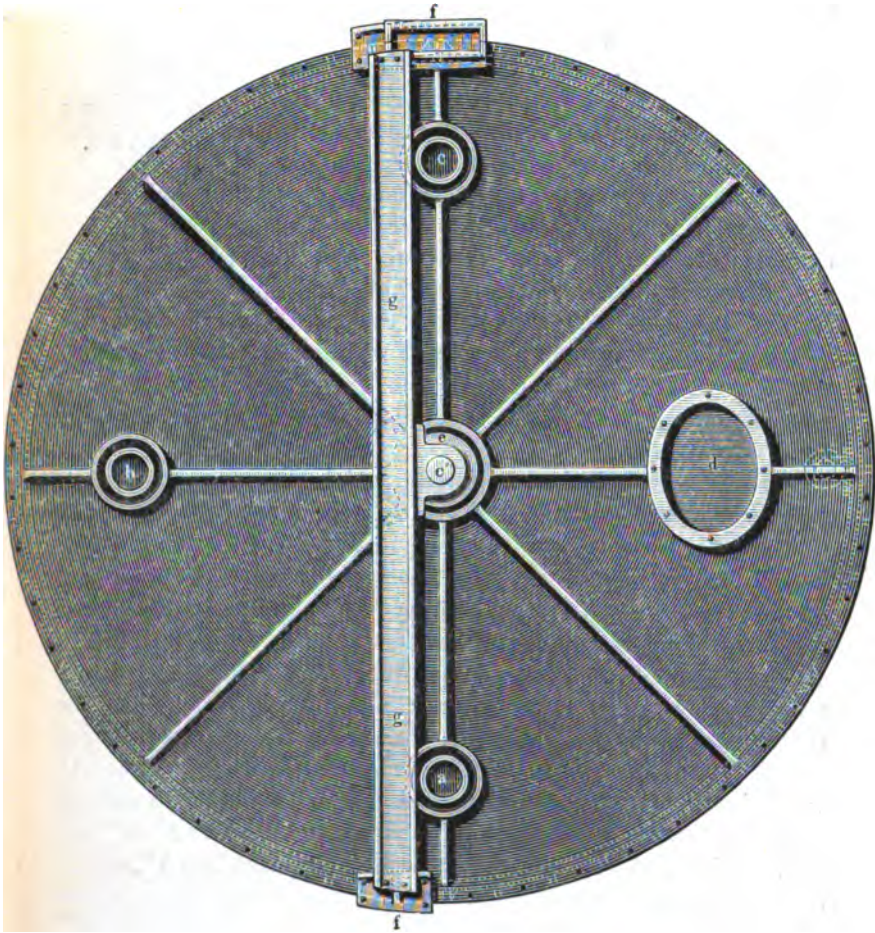


taking away the chlorine; another, *d*, is for the man-hole, *e* for the central agitating-shaft. *a*, *b*, *c*, and *e* are each fitted with two concentric, upright, cast-iron flanges, forming a 6-inch water-lute. When no gas-pipe is connected with them, *a*, *b*, and *c* are closed by caps of cast-iron, earthenware, &c. The oval man-hole



*d* (18 × 15 in.) is fitted with an inner margin of strong sheet-lead reaching 6 or 8 inches downwards and forming a water-lute when the cylinder is filled; apart from this the man-hole is always open, so that observations can be made at any time, samples drawn, and

Fig. 167.



hydrate of lime put in. The central opening, *e*, also forms a water-lute; in this the shaft *h* rotates gas-tight without any stuffing-box, by means of a cup *n* fastened to it. The shaft *h* is made of wrought iron, 4 inches square, turned round in the gudgeons; it is guided by two castings (*ff*) bolted to the top flanges, and a cross-bar *g*,

to one side of which a bearing *e'* is cast; at the bottom the shaft *h* rotates in a footstep. It is set in motion by conical wheels *i* and *k* (2 feet and 1 foot). *k* is attached to a 3-inch shaft, which passes over all the cylinders, by means of a friction-clutch. A two-horse power steam-engine can drive six such agitators. The shaft *h* carries inside the agitating-arms *ll* and *mm*, the former at right angles to the latter; they are made a little slanting, to cut better through the liquid. Each two of them are connected by the cross arms *ll'* and *mm'*; fig. 168 shows a horizontal section of the main shaft, with the arms attached. In the bottom there is a cast-iron 3-inch or 4-inch discharge-cock *o*.

Fig. 168.



Such large cylinders are only adapted for a manufacture on a somewhat considerable scale. Smaller cylinders are usually found at Continental works (say 6 feet in diameter and 3 feet high). They do not, however, seem to work so well as the large ones; for instance, they do not get hot enough without introducing steam, which, again, dilutes the liquid. Small cylinders should have a non-conducting jacket, while in large cylinders such jackets would cause overheating.

Three or more cylinders form a set, which always work together. By means of the 5-inch lead or earthenware pipes *C*, the chlorine can be sent at will into each of the cylinders,—*e. g.* *A'* (fig. 164), by its left-handed water-lute *a*, which corresponds to the water-lute *a'* on the pipe *B*; *a* and *a'* must be joined by a movable double elbow-pipe, or, still better, by the contrivances represented on figs. 103 to 105, p. 294 and 295. The gas issues from *c*, figs. 166 and 167 (*b* only serves in special cases), and passes through a special pipe into the opening *a* of the next cylinder *A''*; from this the gas passes from *c* to *a* in *A'''*, and from this at last by *c* to the small reserve cylinder, *C*, which is also fitted with an agitator, and which stands high enough for its liquor to run into the man-holes of the cylinders *A'*, *A''*, and *A'''*. When *A'* is finished, the fresh gas is admitted into *A''*, and *A'* charged anew; the gas from *A'''* is then taken back to *A'* by the 4-inch connexion-pipe *D*. The cylinders now work in the order *A''*, *A'''*, *A'*; from *A'* the gas again passes by a 4-inch lead pipe to *C*. It is obvious that the work goes on all the more smoothly and well the more cylinders work together; six is a very good number. In this case the chlorine is absorbed almost entirely before it arrives in *C*; but, for the sake of safety, *C* should be connected with a small

bleaching-powder chamber to absorb any gas escaping from the apparatus in consequence of an accidental stoppage of the machinery, too violent an evolution in the stills, &c. The bleach made there is not very well adapted for a commercial article, but is used in the agitators in the place of fresh lime. Where bleaching-powder is manufactured along with chlorate, a branch from the main gas-pipe should go direct to the powder-chambers, to take the gas directly there during any stoppage in the chlorate department.

The absorbers are filled up to 10 inches below their top with water or weak liquors (washings from the mud of former operations); they should not be filled any higher, because the lime takes some space, and the bulk of the liquid is expanded by the heat and by the water condensing from the chlorine; some space must always remain for the gas.

Entirely different from the above, or from any of the apparatus described in the book of Jurisch, is that which is at work at Messrs. Péchiney, at Salindres, and which, according to my personal observations, is superior to all others. It is represented in figs. 169 and 170. Fig. 170 shows a transverse section through one of the vessels. This set, which produces 10 tons of chlorate per week, consists of five vessels, A to E, with semi-cylindrical bottoms and straight sides, about 6 ft. wide, 6 ft. 6 in. high, and 6 ft. 6 in. long. A horizontal agitating-shaft passes through the two straight ends; the blades fixed upon this shaft project above the level of the liquid, which has an excellent effect in forcing the chlorine below the surface of the milk of lime. The shaft turns in plain stuffing-boxes with hemp packing, which, of course, must be pretty frequently renewed. The vessels are made of cast-iron, and are surrounded at a distance of 2 inches by a wrought-iron jacket, which serves for cooling with water—an operation more necessary in the south of France than in England (comp. notes on the temperature, p. 513 *et seq.*). The two bottom vessels, A and B, are on the same level; C, D, and E rise by steps, and all of them are connected in such manner that the contents of the upper vessels can be made to run into the next lower vessel. The fresh chlorine enters either in A or B, mostly in A, and travels on through B, C, D to E; only when A has been run off it goes first into B, and thence forward. The complicated gas-mains and contrivances for changing the currents required in other descriptions of apparatus are quite

Fig. 169.

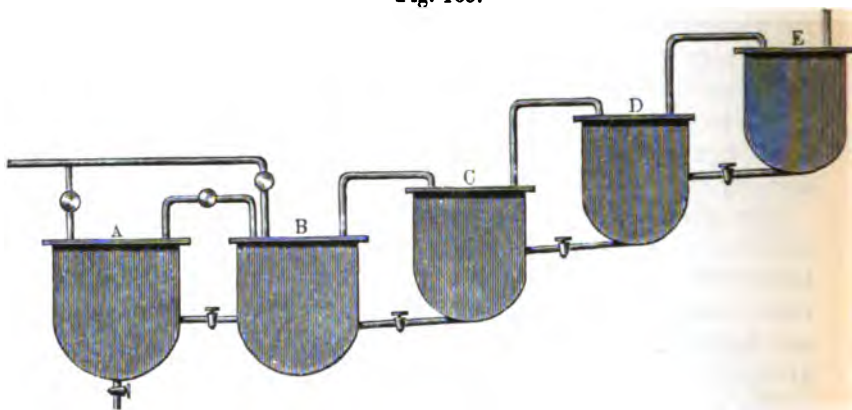
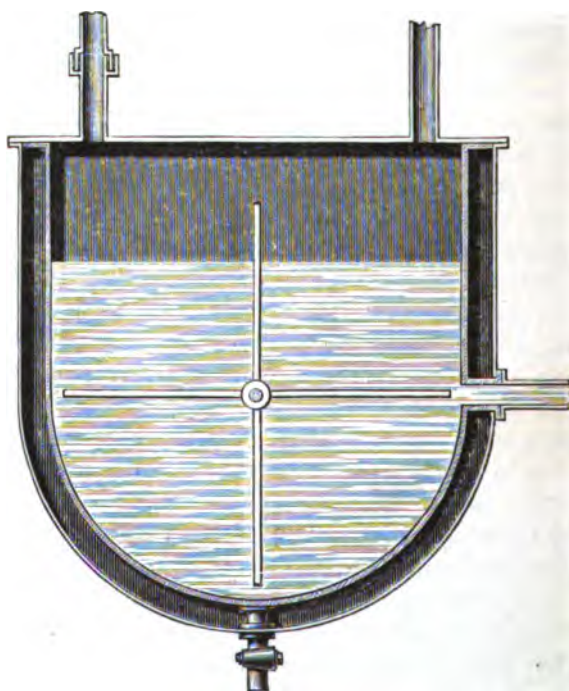


Fig. 170.



absent here. The absorption is excellent; although E directly communicates with the air, I did not notice any smell whatever. As soon as the contents of A are finished they are run off by a bottom tap; then all connecting taps between the five vessels are opened, and at the same time fresh milk of lime is run into E, so that the contents of each vessel are forced into that placed just below. Thus the work goes on with great simplicity and regularity, and the chlorides never exceed 5.5 to 1 chlorate (comp. below).

The *quantity of lime* must be in a certain proportion to that of the water, so that the resulting solution of calcium chlorate shows the proper concentration. According to my experience the best work is done if the finished liquor does not exceed 25° or 27° Tw.; even at 28° Tw. it takes too much time to finish. Jurisch (p. 23) talks of liquor of 33° Tw., but on p. 85 he mentions, that at the Widnes works 29° to 30° was thought best, and 26° to 31° Tw. were considered the outside limits. At the Liverpool works of the same firm they worked to 2° less [which almost exactly agrees with my own experience]. At Kunheim's works, he states, they usually work up to 40° or 44° Tw., at Péchiney's to 42°; but this is probably an error, since Péchiney himself (*loc. cit.* p. 211) states 24° B. (= 40° Tw.), or 60 to 70 grams calcium chlorate per litre, to be the *highest* attainable strength.

According to Péchiney the quantity of lime varies at different works between 50 and 100 grams CaO per litre.

For each cylinder of the size of apparatus shown (pp. 406 and 407) 35 cwt. of hydrated lime are required, which should be thrown through a half-inch sieve. On the first day only 23 cwt., and the next day 12 cwt. of the above quantity are charged; on the third day usually the whole contents of the cylinder are changed into chlorate.

In the regular course of working, the cylinder just charged with lime receives gas at first from an older cylinder, and is finished with fresh gas. As a rule, it heats only when receiving fresh gas, and is then soon finished (in from 12 to 24 hours). At first the liquid is only tepid; then much froth appears in the man-hole, and the temperature rises a good deal. At last the liquid turns pink; and now the froth mostly (but not always) vanishes again. The operation may be considered finished when a sample taken out of the man-hole settles quickly and completely, leaving comparatively

little sediment, and the liquid shows a deep pink colour, smells of chlorine (no longer of hydrochlorous acid), and bleaches litmus-paper. So long as it is not finished (*i. e.* contains hypochlorite) it gives off streams of chlorine when mixed with hydrochloric acid *cold*; afterwards it does not do this. Batches of 24° Tw. usually settle better and of a darker pink than those of 28°. The pink colour is generally ascribed to the formation of permanganate from manganese mechanically carried over or contained in the lime. Opl (Dingl. Journ. ccxv. p. 237) and Blunt (Chem. News, xxxiv. p. 171) assert the colouring-matter to be calcium ferrate; but Davis (Chem. News, xxxiv. p. 183) distinctly asserts the presence of manganese in all pink-coloured solutions of calcium chlorate and bleach-liquor, as well as the direct spectroscopical proof of the presence of permanganic acid. Wagner (Chem. Zeitung, xxxix. 1893, p. 1531) confirms this entirely. When working with materials quite free from manganese, the pink colour is not produced. Bailey and Jones (Journ. Soc. Chem. Ind. 1893, p. 232) arrived at the same result; materials free from Mn yielded no pink solution, even when considerable quantities of iron compounds were added, but at once on adding a trace of manganese. The ferrate theory is thus entirely refuted.

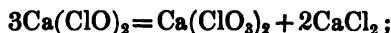
As soon as the contents of a cylinder have been completely changed into chlorate, according to the tests mentioned above, the gas is cut off, and the whole, clear liquor and mud together, is run through the large bottom-cock into the settlers; the cylinder is at once recharged with water or washings and lime, and is now made the last of the set.

When a cylinder cannot be finished all at once, but the work must be interrupted (*e. g.* on account of Sunday), it takes much longer time before the temperature rises and the chlorate is formed. In such cases, heating by steam, which is quite unnecessary otherwise, would be appropriate. A similar thing happens if instead of water or weak washings a concentrated solution is employed, and of course less lime is added; here also the liquid does not heat and will not turn pink. Hence it is best to divide such concentrated liquors, *e. g.* that of the reserve cylinder C, among several absorbers. Without a certain amount of heat no chlorate is formed, but only bleach-liquor:

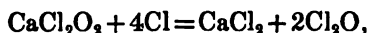


the calcium hypochlorite, when more chlorine is admitted, decom-

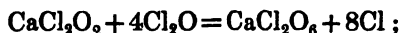
poses into chlorate and chloride with evolution of heat, but without absorbing any more chlorine :



so that, on the whole, 5 molecules of calcium chloride fall to 1 of chlorate. Why this decomposition is complete only when an excess of chlorine is present, and then takes place without much loss of oxygen, is not known with absolute certainty. It is possible to assume that the excess of chlorine with the hypochlorite first forms hypochlorous acid :



and that the latter oxidizes a further quantity of calcium hypochlorite to chlorate, chlorine being liberated again :



but such an assumption of simultaneous absorption and evolution of chlorine in the liquid, although not impossible, can only be maintained on the strength of distinct data, which as yet are wanting.

The process never goes on without some loss of oxygen. According to the equation there ought to be in the finished liquor exactly 1 mol. chlorate to 5 mols. chloride; but it is very rarely possible to get below 5.3 mols. of the latter; 5.4 or 5.5 are still acceptable, but even 5.6 to 5.8 mols. chloride occur to 1 mol. chlorate. In the French works the absorbers are sometimes purposely cooled, to lessen the loss by evolution of oxygen. Since of the 0.3 to 0.5 mol. of calcium chloride in excess a portion is always to be accounted for by the hydrochloric acid never absent from chlorine, very little remains for any chloride formed by loss of oxygen from chlorate; but during the hot French summers possibly more than the above loss may occur unless the liquid is cooled.

Jurisch states (p. 25) that at Muspratt's works the temperature of the chlorate-liquor went up to 35° or 40° C. with Weldon chlorine, or 25° to 30° C. with Deacon gas; the latter always required more time for settling. He considers it wrong to go much above 40° C., as in this case oxygen is lost. I must contradict this, not merely from my own experience (with Weldon chlorine I found a temperature of from 60° to 70° decidedly necessary in order to finish the liquor without too great loss of time), but also

from that gained at the admirably conducted works of Messrs. Péchiney, where I was informed that the process (also with Weldon chlorine) was also conducted at  $65^{\circ}$  or  $70^{\circ}$ , and that it was a rule *never* to remain below  $50^{\circ}$ , because in this case the process either does not make any progress, or else the conversion of hypochlorite into chlorate takes place all at once with an explosion-like speed and great rise of temperature. In his above-mentioned paper (p. 198) Péchiney states that, when the temperature  $50^{\circ}$  or  $55^{\circ}$  has been reached, a froth of oxygen bubbles is seen, all the less the better the operation proceeds. But the temperature of finishing is much higher, viz. about  $70^{\circ}$ , as we shall subsequently see.

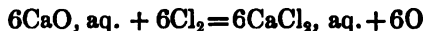
We must go even further. On the strength, firstly, of the observations at Péchiney's works, to be quoted later on, according to which the temperature must rise to  $70^{\circ}$  in order to convert nearly all the hypochlorite into chlorate, and, secondly, of the proof given by myself and Landolt (see below) that, apart from the reducing-action of metals, the loss of oxygen in boiling proceeds exclusively from the decomposition of hypochlorite, not from that of chlorate, we may distinctly lay down the facts of the case as follows :—If the statements of Jurisch concerning the temperatures observed at Messrs. Muspratt's works in "finishing" chlorate liquors were correct, then that manner of proceeding, declared by him to be the right one, must have been extremely irrational, because most certainly at such low temperatures a *large* quantity of hypochlorite must have escaped conversion into chlorate, and very great losses during the boiling-down must have ensued. But the statements of Higgins, mentioned in the description of the magnesia process, prove that Jurisch, in spite of his being so positive, was altogether wrong concerning the temperatures observed at Muspratt's works.

Jurisch (p. 69 *et seq.*) describes, with excessive details, experiments for directly proving the evolution of oxygen in chlorate works, but, according to his own representation, their success was very uncertain. That oxygen *is* formed in this process is notorious anyhow. It can also be safely concluded that such a formation occurs only so long as there is some unchanged hypochlorite present, both from the results of working on the large scale and from Lunge and Landolt's laboratory experiments (see below). It has been observed at Péchiney's works that the air escaping from



the apparatus described above (p. 509) is rich enough in oxygen to make a glowing match burst into flame.

The *heat of formation* of potassium hypochlorite in aqueous solution,  $2\text{KOH, aq.} + \text{Cl}_2 = \text{KCl, aq.} + \text{KOCl, aq.}$ , is 24.6 cal.; that of potassium chlorate,  $6\text{KOH, aq.} + 3\text{Cl}_2, \text{aq.} = 5\text{KCl, aq.} + \text{KClO}_3$ , is 97.9 (Fischer, *Zsch. f. angew. Ch.* 1888, p. 551). The first sum must be multiplied by 3, to compare it with the second: this gives  $97.9 - 73.8 = 24.1$  cal. as excess of heat evolved on the transition from hypochlorite into chlorate. This would lead us to expect that this transition takes place without a supply of energy from without. This is not the case directly, but by taking the roundabout way of employing an excess of chlorine (which is again recovered in the end), the conversion may be effected up to 70 per cent. *in the cold* (see below). The reaction

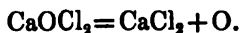


gives off 118 cal., that is 21 cal. more than the conversion into calcium chlorate. Here again thermochemical considerations do not allow us to predict the course which the reactions actually take.

An extensive investigation on the *conversion of calcium hypochlorite into chlorate* has been made by Lunge and Landolt (*Chem. Ind.* 1885, p. 343; *Journ. Soc. Chem. Ind.* 1885, p. 722). When heating a solution of chloride of lime by itself, the conversion into chlorate is very imperfect. After 3 hours' gradual heating to 60° C. it is hardly perceptible; it becomes so only after further heating to 70° for an hour; stronger after 2 hours' heating to 90°; but even after another 2 hours' heating to actual boiling not much over  $\frac{1}{4}$  of the chlorine had been utilized for the formation of chlorate. As soon as some chlorate is formed, an excess of chloride is found, which points to a loss of oxygen, and in the end the latter reaction prevails altogether; while 27 per cent. of the original chlorine had been consumed in the reaction



30 per cent. had entered into the reaction



Hence the conversion of hypochlorite into chloride by heat alone is a very expensive process.

The effect was totally different on heating a solution of bleaching-

powder saturated with free chlorine. Even in passing chlorine into the cold solution at 15° C., 70 per cent. entered into the formation of chlorate; this proportion did not perceptibly increase after long standing, and not very much on warming up to 40°. On gradual heating up to the boiling-point the conversion is complete; it should be observed that even after two hours' boiling no loss of oxygen was noticed, so that this must have been prevented by the excess of chlorine. In a further series of experiments we did not satisfy ourselves with once for all saturating the solution with free chlorine, but passed it in, during the whole process; we did not observe any hastening of the formation of chlorate by so doing, and this is easily understood, since the reaction does not require a supply of more chlorine.

We arrived at the following conclusion:—The most favourable conditions for the conversion of hypochlorite into chlorate are not presented either by simply raising the temperature alone or by a mere excess of chlorine: *both of these must act together*. A large excess of chlorine offers no advantage; rather the contrary. On the large scale it is unnecessary to heat the liquor on purpose, as the heat evolved by the reaction itself is sufficient. Great harm is done by heating in the absence of free chlorine, because this leads to the evolution of much oxygen and formation of chloride, which seems to be prevented by the excess of chlorine.

We found that *finished* chlorate liquor does not lose any oxygen even on prolonged boiling, unless the action of metals (see below) or other reducing substances comes into play; the decomposition otherwise only extends to hypochlorite. This explains an observation of Parnell's, quoted by Muspratt (Journ. Soc. Chem. Ind. 1886, p. 408), according to which solutions containing free lime lose much chlorate on boiling, with evolution of oxygen. It is not the presence of lime itself which causes that loss, but the circumstance that solutions of this kind, which are, of course, imperfectly saturated, contain much undecomposed hypochlorite. Since they always contain at the same time some ferric oxide, &c., the decomposition of the hypochlorite is quickly brought about on boiling, and the liquors in the end suffer a corresponding loss of chlorate.

Péchiney (*loc. cit.* p. 199) gives a very instructive table showing the progress of the process (with Weldon chlorine). It refers to samples from large-scale work, taken from the first of the vessels of the apparatus described on p. 509. As there shown, this

vessel (A) receives from C a liquor already partially converted into chlorate. The operation embraced about 140 cubic feet; the outer temperature was 12° C. The results are calculated upon 1000 equivalents of the chlorine *finally* contained in the liquor, and we can see therefrom the state of the chlorine during the successive stages. The observations were made at each rise of 5° C. in temperature.

Number of observation.	Minutes after the entrance of the liquor.	Temperature ° C.	Total equivalents of chlorine absorbed.	Equivalents of chlorine as hypochlorite.	Equivalents of chlorine as chlorate.	Equivalents of chlorine as chloride.	Equivalents of chloride to one of chlorate.
1. ....	...	38	660.2	315.6	52.52	291.9	5.55
2. ....	10	43	762.50	432.20	50.10	280.2	5.58
3. ....	18	48	852.26	506.76	53.3	292.2	5.54
4. ....	24	53	925.40	578.4	53.3	293.7	5.50
5. ....	28	58	954.50	329.9	97.1	527.5	5.42
6. ....	32	65	985.50	66.9	148.1	770.5	5.20
7. ....	33	70	1000	15.7	157.4	826.7	5.24
8. ....	36	70	1000	11.9	158.1	829.9	5.24
9. ....	40	70	1000	11.9	158.1	829.9	5.24

*Observations.*—No. 1 is the liquor coming from the vessel C, which already contains some chlorate, although the temperature never rises above 40° there, but principally hypochlorite.

Nos. 2 and 3 show that at this stage, up to 48°, exclusively hypochlorite is formed; in consequence of the increase of bulk of the liquid, the apparent percentage of chlorate is even decreasing.

No. 4. At 53° the oxygen froth begins to appear, the hypochlorite still increases; *the formation of chlorate has made hardly any progress* (pp. 513 and 514).

Nos. 5 and 6. Rapid rise of the temperature from 58° to 65°; rapid conversion of hypochlorite into chlorate.

No. 7. At 70° the operation is finished; the hypochlorite has almost vanished; the liquid is pink-coloured.

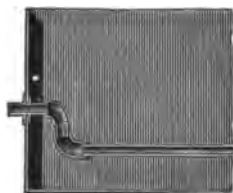
Nos. 8 and 9. Although the supply of chlorine gas continues, there is no change of temperature nor in the composition of the liquor; the chlorine now passes over without any change into the second vessel.

*Settling the Liquor.*

The *settlers*, E E (figs. 164, 165), are best built up of cast-iron plates; when made of wood and lined with lead they are liable to be often needing repair. They are placed so much lower than the absorbers that they can be filled from any of these by means of a large spout with plug-holes. More settlers are needed if the mud is washed in the settlers themselves than if only the clear liquor is run off and the mud washed in different vessels. The clear liquor is run off by means of a swivel siphon inside the settler, similar to those mentioned in other places. The swivel pipe is kept in its place by a chain or a thin curved iron rod. Fig. 171 shows a double swivel for lowering the pipe parallel with the front of the settler, as seen from above; fig. 172 is a perforated drum surrounding the mouth of the pipe and covered with canvas, by means of which the liquid can be drawn off lower down without carrying away any mud. An iron spout running along all the settlers takes the clear liquor from all the pipes to a well, I (figs. 164, 165), from

Fig. 172.

Fig. 171.



which a pump, H, pumps them into the higher tanks K or L. But rarely can the absorbers be placed high enough for giving a fall not only to the settlers, but also from these to the pans, and from these to the crystallizing-coolers; by such an arrangement the pumping of the strong liquors is saved, but not that of the washings, which have to go back into the absorbers. The well, I, must have two partitions, I' and I'', so as to keep the strong liquor always separate from the washings: the former only is sent into the pans; and its volume must be accurately known. The height of the strong liquor before and after running it off from E, and thus the bulk of the liquor sent into the tanks, is ascertained—which is absolutely necessary in

order to calculate the amount of potassium chloride (muriate) to be added. After running off the strong liquor, the *mud* is either discharged into other vessels for further treatment, or, as we have assumed in the drawing, it is washed with water in E itself, so long as the hydrometer shows any salt in the liquor; and the washings, run into I'', are pumped into the reservoir L, from which they are taken as wanted, instead of part of the fresh water, for charging the cylinders A. The washed mud is discharged through a plug-hole in the bottom of the settler, or by shovelling out; it consists of silica, clay, calcium carbonate, and a little calcium hydrate, and is of no further use. The operation of washing it would be very much simplified and improved by employing a filter-press; and the same holds good of the muddy residues obtained afterwards in the boiling-down pans and the dissolver for crude salt.

Incompletely finished liquor, containing excess of lime, settles very badly.

Instead of measuring the chlorate liquor before running it into the boiling-down pans in the settlers themselves, this can of course be done in special measuring tanks placed between the settlers and the pans. This is unavoidable if the shape of the settlers makes it too difficult to perform the measuring therein; but it has always the inconvenience of requiring more fall for the liquor.

### 3. *Boiling-down the Chlorate Liquor and addition of Potassium Chloride.*

The clear solution of calcium chlorate and chloride must now be boiled down. Formerly the *boiling-down pans* were made of lead, and consequently subject to the rapid wear and frequent damage incidental to this material. Here also, as well as in every other portion of the plant for manufacturing crude chlorate, lead has been replaced by cast iron or even wrought iron, without damaging the quality of the chlorate, which must in any case be recrystallized.

The choice can only be between wrought-iron or cast-iron pans. The latter have certain advantages, especially in being less acted upon by the liquor: but the former are cheaper, can be made of all sizes, and are not liable to crack; so that they are decidedly preferable, and the more so if the free chlorine, which alone could damage them, is removed by adding a very small quantity of soda-waste to the liquor run out of the pans, as this instantly destroys

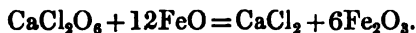
its smell and colour and prevents any corrosion afterwards of either the pans or the pumps.

The pans have the same shape as the "boat pans" described in Vol. II. pp. 647 to 649, and are set exactly in the same manner. They ought to be covered with planks and possess a draught-pipe to carry the chlorine given off at first to the chimney; but this is quite unnecessary if the above-mentioned treatment with tank-waste has been carried out. Two pans 8 ft.  $\times$  20 ft.  $\times$  3 ft. suffice for the apparatus described; their waste heat passes underneath the small pans Q Q (figs. 164, 165), which are placed at a higher level and serve for dissolving the crusts and mud from the pans P P, the dissolving residue, and the washings from refining, and running the clear liquor into the pans P P; as this liquor already contains *potassium* chlorate, not calcium chlorate, it must be sent directly into the pans. The pans P P are run off by swivel pipes, just like the settlers E E.

#### *Addition of Potassium Chloride.*

We have already seen that the volume of the clear liquor sent from the settlers E into the pan is gauged. At the same time a sample is taken, tested for chlorate in the laboratory, and the addition of potassium chloride calculated from this test. One might think that, if the quantity of lime charged into the absorbers remained the same, or, at least, if the specific gravity of the clear liquor in E were the same, there would be always the same quantity of potassium chloride required for effecting the decomposition. But this is not the case; and as the potassium chloride (or, to call it by its commercial name, the *muriate of potash*) is the dearest of all the raw materials employed, it is not advisable to add any considerable excess. Still less will it do to add too little; for any calcium chlorate, being very soluble, would remain in the mother liquors. There are many processes for estimating chlorate; but the following is probably the easiest and quickest. A solution of about 100 grams of pure crystallized ferrous sulphate and 100 grams strong vitriol is made up to one litre, and its value ascertained by daily titration with seminormal potassium permanganate (*i. e.* one containing 15.82 grams pure crystallized salt per litre, and indicating 0.004 gram oxygen per cub. cent.). Suppose that each 25 cubic centims. of iron-solution require 20.5 of permanganate, a certain quantity of the chlorate-solution is pipetted into a flask, boiled till all free

chlorine is expelled, cooled, and a sufficient quantity of iron-solution added, the flask closed, with an india-rubber cork and a Bunsen's valve, or with a twice bent tube, the outer limb of which dips into water contained in a beaker; heat is applied, the liquor kept fully boiling for a few minutes and then cooled, during which the closing of the valve or the coming back of the water from the beaker prevents any oxidation by the atmospheric oxygen. All the chlorate is now converted into chloride or sulphate; and a corresponding quantity of ferrous sulphate is converted into ferric sulphate:



All the oxygen of the chlorate is spent in peroxidizing the iron salt.

The liquor is now retitrated with permanganate; thus the quantity of ferrous sulphate consumed, and consequently that of the chlorate, is found. The permanganate corresponding to the chlorate (*i. e.* that required for standardizing the iron-solution, less that consumed in retitrating) shows the amount of the chlorate at once by a simple factor, and that of the necessary potassium chloride by another. As seminormal permanganate solution (*i. e.* a solution of 15.82 grams  $\text{KMnO}_4$  in 1 litre of water) gives off 0.004 oxygen per cub. cent., and since 122.6 parts of  $\text{KClO}_3$  yield 48 of oxygen, the former must show per cubic centim.  $\frac{122.6}{12}$

$= 0.01021 \text{ KClO}_3$ , or  $0.00621 \text{ KCl}$ . Suppose the commercial muriate employed to contain 95 per cent.  $\text{KCl}$ , the last factor will become  $\frac{0.00621 \times 100}{95} = 0.006537$ . Hence, if 2 cub. cent. of the

chlorate liquor have been employed, if this has taken up iron equivalent to 15.5 cub. cent. permanganate, each litre of the liquor will correspond to  $15.5 \times 500 \times 0.01021$  gram  $\text{KClO}_3$ , and will require an addition of  $15.5 \times 500 \times 0.006537$  grams of 95-per-cent. muriate. If the calculation is to be simplified still more, the factor is made to contain once for all the number of litres per centimetre (or inch) of the height gauged. If the settlers were exactly  $3 \times 2$  metres, each centimetre of their height would be  $= 60$  litres; hence, if for each testing 2 cub. cent. of liquid are taken, the constant factor for 95-per-cent. muriate upon a consumption of  $x$  cub. cent. permanganate becomes  $x \times 500 \times 60 \times 0.006537 = 196.11 x$ . That is, for each cub. centim. of perman-

ganate used in testing 2 cub. centims. chlorate liquor, each centimetre of the height of the settlers requires 196·11 grams 95-per-cent. muriate of potash. It will be easy to apply this calculation to any given size of settler, and to English instead of metrical measures.

This calculation shows at the same time in stock-taking how much loss there has been in crystallizing, refining, &c.; it points out, and frequently permits stopping, any sources of loss.

There is always some excess over the theoretical quantity of potassium chloride added, to compensate for any inaccuracy of reading off the height of the acid, &c.; an addition of 3 per cent. above the calculated quantity will suffice in most cases. It is decidedly advisable to employ the purest muriate, nearly free from sodium chloride, in spite of its comparatively higher price; for all this sodium chloride gets mixed with the potassium chlorate, renders it more difficult to be purified from chlorides in refining, and causes loss by increasing the quantity of mother liquors. Upon 10 parts of potassium chlorate actually obtained,  $8\frac{1}{2}$  to 9 parts of good muriate of potash are needed (comp. further on).

Jurisch states that at Muspratt's works, before the mother liquors were worked for chlorine, at first rather less than the theoretical quantity of KCl was added, in order to avoid any loss of it, but this was subsequently abandoned—evidently because the yield of potassium chlorate was too much impaired. We shall have occasion to refer to this again.

The potassium chloride was formerly sometimes added already in the absorbing-cylinders, but now this is done only in the boiling-down pans; in the former case, of course, the muriate cannot be calculated exactly. The opinion occasionally held, and probably forming the ground of this method, viz. that calcium chlorate inclines more to decomposition than potassium chlorate, is entirely unfounded.

The potassium chloride required for a batch is put into the pans directly after running-in the first portion, or, still better, as soon as this has been brought to ebullition; and the boiling-down is continued, feeding the pan with fresh liquor either continuously or by instalments, till the proper degree of concentration has been attained. The procedure is not the same in all places. Some evaporate the liquor at once down to 70° Tw. (measured hot) and allow it to crystallize; the mother liquors then contain so little chlorate that they cannot be worked for it. Others only boil



down to 50° or 55° Tw., and after crystallization evaporate the mother liquors once more to 71° Tw. By the latter plan perhaps a little more chlorate is obtained; but it is doubtful whether the increased labour, consumption of fuel, and mechanical losses do not outweigh that advantage. The second portion of salt is very impure, and must be recrystallized twice, while the first plan (which we will describe in detail) requires only one recrystallization of all the salt.

Jurisch states (p. 37) that at Muspratt's works the first liquor was boiled down in summer to 62–68°, in winter to 58–64° Tw. (measured moderately hot). The mother liquor from the first crystallization was further evaporated in summer to 78–85°, in winter to 72–78° Tw. (measured moderately hot). The mother-liquor crystals were re-dissolved to 40° Tw. and yielded crystals of the same quality as otherwise obtained from the first boiling. Centrifugalled crude crystals tested 84–88 per cent.  $\text{KClO}_3$  and 2 per cent.  $\text{CaCl}_2$ , besides water and mud (p. 97).

According to Jurisch's calculations (p. 90) there must be an extraordinarily great loss of chlorate in boiling-down by the decomposition of chlorate. In a case detailed by him the proportion of chloride to chlorate in the crude liquor was 6.0 : 1, in the boiled-down liquor 13.44 : 1, from which a loss of 44.7 per cent. of chlorate is calculated. Such a loss he himself calls unusually high, since otherwise the *total* loss, including mother liquors, is only 30 per cent. He opines that this enormous loss was due to the fact that in the above case the evaporation was at once carried to 74° Tw., instead of dividing the concentration into two stages; but this must be wrong, since at other works where the boiling-down is performed all at once, they never notice anything like such losses. Jurisch himself considers the average loss in boiling-down to be between 10 and 20 per cent. The cause of this loss, so far as it is not due to the presence of hypochlorite (p. 516), is the action of the metal of the pans on the chlorate.

According to experiments made in my laboratory (Journ. Soc. Chem. Ind. 1885, p. 32) concentrated solutions of potassium chlorate, and even more so the mixed chlorate liquor produced in the process, act upon lead, wrought iron, and cast iron. Calculated upon the weight of the metal dissolved, the action is least in the case of cast iron, slightly greater with wrought iron, and greatest with lead. Calculated upon the weight of the chlorate of potash

destroyed, the difference in the case of mixed liquor is not very great; in fact it is slightly in favour of lead; but as the loss of lead is 5 or 6 times greater than that of the other metals, and the cost of firing and repairs is also much greater than with iron, the latter is decidedly preferable as material for boiling-down pans.

Aqueous solutions of potassium or calcium chlorate, according to my experiments, are not in the least decomposed by boiling in glass, porcelain, earthenware, &c. Unfortunately these materials are hardly available for manufacturing use.

At P  chiney's works, just as was done at mine, the liquor is at once boiled down to 74   Tw. (measured hot); per cubic metre of the concentrated liquor about 130 kil. crude salt is obtained, with 95 per cent.  $\text{KClO}_3$ , 0.55 per cent.  $\text{CaCl}_2$ , and 4.45 per cent.  $\text{H}_2\text{O}$ . Nothing has been observed there of the great loss in this style of boiling-down, as compared with doing it in two stages according to Jurisch. They have found there that the action of the liquor on the (wrought-iron) pans, together with loss of chlorate, is very much stronger if magnesian limestone is used, in which case during the concentration magnesium chloride is formed. Therefore the employment of pure limestone greatly diminishes that loss.

When the pans are run off, the mud is best kept back by means of a filtering-drum (fig. 172): it must be taken out after each operation, lest it burn fast to the pan and cause it to wear out prematurely. The mud is washed in the small pans Q (figs. 164, 165), and the liquor boiled down in the pans M along with the other liquors. The discharge-pipes of the pans M join into an open spout, from which, by means of branch spouts, all the *crystallizing-cones* N N can be filled.

#### 4. *First Crystallization of Chlorate.*

A sufficient number of crystallizing vessels should be provided, to permit the liquor to remain in them 9 or 10 days in winter, and 14 days in summer. Formerly they were made of wood and lined with lead; but cast iron is preferable, as with care it does not contaminate the salt much more; and it is far better than lead vessels, in consequence of its greater conductivity for heat and its immunity from leaking. The iron vessels are made exactly like those employed in making soda crystals, viz. large shallow pans, or oblong pans with rounded corners (Vol. II. p. 706).

They ought to be placed at a slight elevation above the floor, and provided with a plug in the bottom for running out the mother liquors. On the ground between each two rows of them spouts are laid to receive the mother liquors, which they convey through several wells P P, sunk in the ground for the purpose of catching the salt always carried away. The larger these wells are, and the longer the mother liquors remain in them, the more completely can the fine crystals of chlorate settle; and even the continued cooling acts favourably in this respect. A canvas filter in front of the drainage-pipe is also very useful for retaining small crystals. The salt collecting in the catch-wells is mostly too impure to be refined directly, and is either simply put back into the pans M M, or else it is recrystallized once more.

When the time is up, the plug in the bottom of each crystallizing-cone is lifted, at first gently, so that but little salt gets out along with the mother liquors; most of this can be retained by a canvas bag suspended below the plug-hole. If no plug-hole is provided, a lead siphon is employed, the outer limb of which does not end in the spout, but in a bucket, where a good deal of salt is caught. When most of the mother liquor is run off, the salt, which is easily detached from the sides, is heaped up round the plug-hole, allowed to drain, and then put into special *drainers* O O (fig. 164), made of wood, lined with lead, with a perforated false bottom. These drainings run away along with the former mother liquors, with which they are identical in composition; but afterwards the adhering mother liquor and mud is washed off by pouring water over the salt from a watering-can, and as some chlorate will be dissolved now, these washings are run into a separate well and pumped back into the pans. This work is much better done by a small (even a hand-worked) centrifugal machine, in which the washing and draining are effected much more completely. The washing is greatly facilitated by the stoutly acicular shape of the crude crystals. If among these are large, clear, transparent prisms of hydrated calcium chloride, this proves that the boiling-down has gone too far, which happens most readily in winter time, and must be remedied by concentrating to one degree of the hydrometer less. The washing is not continued very long, in order that there may not be too many diluted liquors; but if it be interrupted too soon, the liquors will have to be changed all the sooner in recrystallizing.

The *mother liquors* ought, before running to waste, to be regularly tested for their percentage of calcium chlorate and of potash. Of the former (calculated as  $\text{KClO}_3$ ) the maximum usually present is 25 grams per litre (Jurisch says, 25 to 35 grams), or 25 ounces per cubic foot; the best result known to myself is 17.5 grams. But with bad work 35 grams per litre and upwards are found, which means a considerable loss. When too much chlorate is present, this may be caused by insufficient evaporation or by the cooling not having lasted long enough. But it may also be caused by a deficiency of potassium chlorate permitting calcium chlorate to remain undecomposed; this is discovered by an estimation of the potash (with platinum chloride), which should show at least 10 grams  $\text{KCl}$  per litre in excess of that required by the chloric acid present. But it also happens that on putting the muriate into the pans the men do not stir it up enough, so that a portion of it may remain at the bottom and afterwards be wanting in the liquor.

At Péchiney's works in the South of France the mother liquors are not run away in summer time, because too much chlorate would be lost in this way. They are kept in large tanks until the cooler season, and yield thus still 8 grams chlorate per litre. Even then 25 to 30 grams  $\text{KClO}_3$  per litre is left in solution, together with 525 to 550 grams  $\text{CaCl}_2$ .

Wylde, Hammill, and Auer (Engl. pat. 15097, 1888) go still further in this direction. They expose the mother liquors, testing  $72^\circ \text{Tw.}$  with the lime process, or  $51^\circ \text{Tw.}$  with the magnesia process, to a temperature of  $-18^\circ \text{C.}$  during a week, which causes a large quantity of chlorate of potash to crystallize out. By further cooling also the calcium (or magnesium) chloride, with 6 molecules of water, is separated. Hammill (Journ. Soc. Chem. Ind. 1888, p. 168) describes this process in detail. The solutions must not be subjected to the cooling process at a greater concentration than the above, because otherwise the chloride also crystallizes from the first. The crude crystals thus obtained have a much finer grain than ordinary crude crystals, but are not more impure (2.4 per cent.  $\text{KCl}$  and 0.9 per cent.  $\text{CaCl}_2$ ). They are quite as easily refined by one recrystallization. On cooling down to  $-12^\circ \text{C.}$  only 13.5 grams  $\text{KClO}_3$  remain in the liquor, equal to a loss of 12.9 per cent., whereas in the ordinary process the loss is at least 25 grams = 24 per cent. By stronger cooling the loss can

be still more reduced, and an increase in the yield of about  $\frac{1}{4}$  can be attained. Hammill calculates the cost of this extra yield of 1.45 tons of chlorate, in a weekly make of 10 tons, to amount to no more than £4 5s.

According to further information concerning this process, starting with a liquor of spec. grav. 1.352, containing 28.5 grams  $\text{KClO}_3$  per litre, and cooling it to  $-21^\circ\text{C}$ . during  $3\frac{1}{2}$  days, 19 grams of crystals are obtained, and only 9.5 grams are left in the liquor. When exactly calculating all costs, inclusive of interest and depreciation on plant of the value of £1200, of the loss of ammonia from the ice-machine, packages, shipping expenses, &c., the 34 cwt. gained upon a weekly make of 10 tons cost in all £11, and leave a profit of £60, that is £6 per ton of the total make.

Kynaston (Engl. pat. 14344, 1886) proposes removing from these mother liquors a large portion of the  $\text{CaCl}_2$  as oxychloride, by adding lime to it, and to obtain more potassium chlorate from the filtered liquor by concentration and cooling. (This treatment was patented before him by Péchiney, who had practically applied it only to sodium chlorate.)

Many attempts were formerly made to utilize the *chlorine* contained in the chlorate mother liquors by boiling them with hydrochloric acid (comp. our first edition, vol. iii. p. 311); but this method was soon abandoned, because it did not pay for the expense and trouble. Sometimes the evolution of chlorine took place explosively, with such danger to all who happened to be in the vicinity that these experiences acted in a very discouraging way. Jurisch states (p. 42) that in 1878 this process had been revived. A Weldon still was employed for this purpose, which was filled  $\frac{1}{10}$  or  $\frac{1}{8}$  with hydrochloric acid of  $26^\circ$  or  $28^\circ\text{Tw.}$ ; then the mother liquor was slowly run in, and steam was blown in *at once*. If this was neglected, and the steam was applied too late, the above-mentioned explosion-like evolution of gas took place. When the still was filled to  $\frac{2}{3}$  or  $\frac{7}{8}$  of its height, the liquor was shut off, and the expulsion of the chlorine was completed by steaming. The liquor, which was kept acid to the end, was run to waste. Each operation took from 24 to 30 hours [which means a somewhat considerable quantity of steam!]. In this case they added a little less than the theoretical quantity of  $\text{KCl}$  to the chlorate liquor before boiling-down, in order to lose

less of it, so that the mother liquor contained a little undecomposed calcium chlorate. [This was soon given up again.] Jurisch (p. 122) states that 1 ton of chlorate could be made from mother-liquor gas to every 5 tons made from Weldon chlorine.

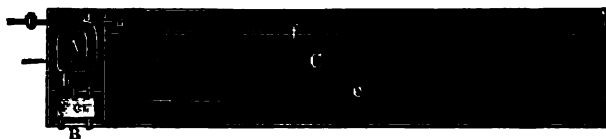
The explosions ascribed by Jurisch to violent evolution of chlorine are, according to Journ. Soc. Chem. Ind. 1887, p. 250, probably caused by chlorine peroxide, as indicated by its phosphorescence.

### 5. *Recrystallizing (Refining) the Crude Salt.*

The crude salt is not a commercial article; its colour, sometimes nearly white, but often brown or reddish, the shape of its crystals, and its chemical impurities, necessitate its purification by dissolving, settling, and recrystallizing, mostly followed by washing the crystals. One of two plans is followed here. In the one the dissolving and crystallizing are one continuous process; in the other they are successive operations.

The first (continuous) method is carried out as follows:—A wooden cistern lined with lead (fig. 173) 40 feet long,  $7\frac{1}{2}$  feet wide,

Fig. 173.



and  $1\frac{1}{2}$  foot deep, is divided into three compartments, A, B, and C. A ( $4 \times 5\frac{1}{2}$  feet) serves for dissolving; B ( $4 \times 2$  feet) for filtering; the largest compartment, C, for crystallizing. In A there is a lead steam-pipe *a*, which is laid in several coils and comes out sideways, carrying out the condensed water; in this compartment the crude salt is put, either on a sieve or in a bag, and is dissolved by heating with indirect steam in the mother liquor coming over from C through the siphon *d*. Thus at the bottom of A a hot saturated solution collects, which is continuously pumped by the small pump *b* over the sieve *c* (covered with very densely woven calico) into B. Since pumping cannot be avoided here, and the application of steam-power is not well adapted for such light work, a contrivance driven by water-power is employed (which is shown in fig. 174).

To the roof two hangers, *b*, are fixed, with rings in which a flat iron rod, *a*, with pivoted ends, turns. *a* carries on one side the arm *c*, to which the plunger *d* is suspended. This is made of

Fig. 174.

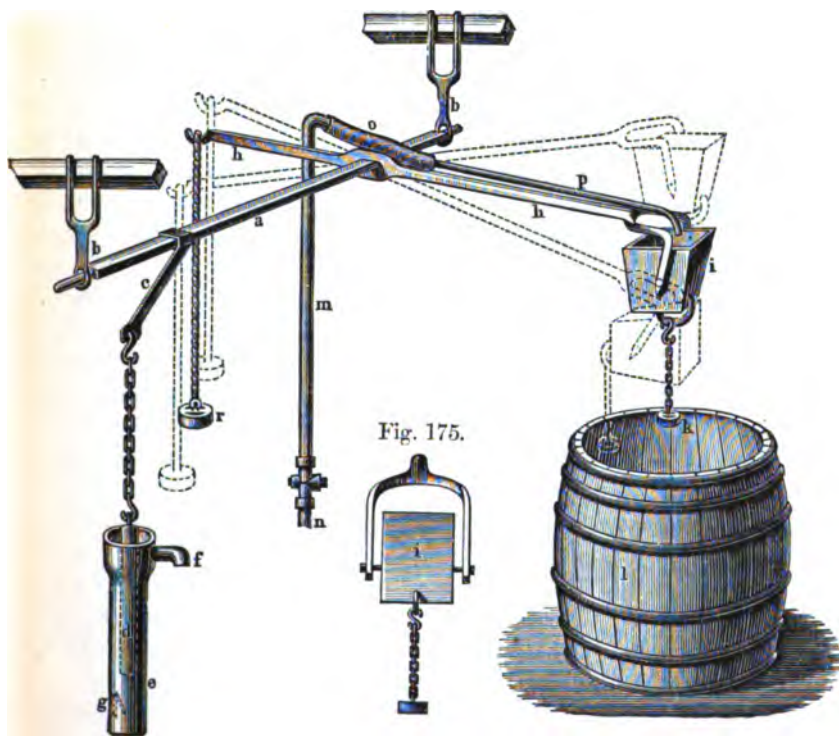


Fig. 175.

wood, covered with lead, and travels loosely in the small pump-barrel *e*, closed at the bottom, with an outlet-pipe *f* at the top and inlet-valve *g* near the bottom. The latter need not close tightly; it is only made of a round piece of india-rubber a little larger than the aperture in *e*, hung from a nail above the latter, and stiffened at the back by a bit of lead. The iron rod *h* is fixed in the same horizontal plane as *c*, and sends out arms on both sides of *a*. On the side opposite to *c* it carries, in a fork curved downwards, the tipping bucket *i*, which is shown separately in fig. 175. Its pivots are below its centre of gravity, so that, when empty, it hangs down straight with the assistance of the small weight *k*.

But when *i* is filled with water so far that the centre of gravity is above the pivots, its equilibrium becomes unstable, the bucket tips over, empties itself, and at once rights itself again by means of the weight *k*. The water for filling the bucket runs from the regulating cock *n*, through the pipe *m*, connected by a flexible tube *o* with the stiff tube *p*, which has an outlet into the bucket *i*.

The apparatus works in this way:—When the cock *n* is opened, the bucket *i* is gradually filled with water and becomes heavier. As the rod *a* turns in the rings *b*, the bucket *i* will go down and turn the rod partly round its axis; the flexible connexion at *o* permits the water-pipe *p* to follow. At the same time the arm *c* rises, and along with it the plunger *d*. Consequently liquor will run into *e* by the valve *g*. As soon as *i* has arrived at the lowest point, it tips and then rights itself again; and this side is now so much lighter than the other, that the rod *a* suddenly turns back. In order to assist this a weight *r* is suspended by a cord from that arm of *h* which is on the same side as *c*. This, together with the weight of *d* itself, causes *a* to turn suddenly, and at the same time *c* to go down, and *d* to enter the barrel *e*. By this a certain quantity of liquid is forced out of *f* into its place of destination.

The length of rope is so regulated that the weight *r* strikes upon the floor or upon a bracket, &c., before *d* has descended quite to the bottom of *e*: this prevents damage to the latter by the sudden shock. Immediately afterwards the bucket *i* begins to fill again, and the process begins anew. The water running out of *i* and that running out of *p*, during the tipping run into the tub *l*, and may be used for any purpose.

A special advantage of this kind of pump is, that travelling ever so slowly it can never "lose its charge." By regulating the cock *n* the filling of *i* can be hastened at will; and this regulates the number of strokes. The quantity of the liquid running out is regulated by the plunger *d*, which can be made to dip more or less by means of its chain. This apparatus works very well and gives no trouble.

The hot chlorate liquor, pumped in this way into B (fig. 173), and filtered through *c*, can enter from B into C by a 1-inch aperture at about  $\frac{1}{3}$  of the height of the latter. In C it is forced by the board *e* to travel to its other end and forward again before it can get to the siphon *d*, also kept apart by a board *f*. Since only about half a gallon of liquid is sent every two or three minutes



into B, this small quantity does not cause any sensible disturbance or current in the large space of C; on the contrary, the liquid is quickly cooled there, and gradually deposits crystals, which constantly grow, and become largest in the part furthest from the compartments A and B. When the liquor has arrived at the siphon *d*, it is quite cooled down and is drawn off by the latter (which is constantly filled, and the orifice of which in A is narrowed down to  $\frac{3}{8}$  inch) into A at the same rate as the pump sends hot liquor over into B.

Thus the work is perfectly continuous; the mother liquor, saturated in A with crude salt, is pumped into B, filtered, run through C, cools there, deposits its excess of salt in a pure form, and returns through the siphon *d* just in the proportion as it is wanted. Once a week the salt accumulated in C is fished out (with a shovel of hard wood or copper); it is best to cease dissolving a day before. From time to time, when the mother liquor has become too impure, it must be pumped back to the boiling-down pans for crude salt, and fresh water must be put into the dissolver. This ought to stand on a water-tight floor, and be a little raised, so that, in case of leakage, the liquor running out may be saved.

This plan of crystallization is best adapted for crude salt deprived almost entirely of mother liquor, and also for salt obtained by evaporating to only 50° or 55° Tw.; it takes but little labour and supervision. But it is not so well adapted for suddenly increased or decreased demands upon the production; hence it is not so much to be recommended as the second, discontinuous plan (*dissolving in special vessels* and slowly crystallizing), in which the concentration can be regulated at will and larger crystals can be made.

In this case the crude salt, already deprived of mother liquor, is dissolved by water and steam in iron or wooden cylinders lined with lead, about 6 feet wide and high. It is best to surround iron vessels with a non-conducting jacket. The steam is not employed directly, but in a coil of lead pipe, passing outwards again; its waste portion may be used for heating the drying-plates (see below).

The liquor is run off best by a swivel pipe, the top of which carries a perforated drum (p. 518) with a double canvas cover, as here every impurity must be kept out. Each such tank can dissolve 6 or 7 cwt. of crude salt. The liquor is made up to 25° Tw.;

at 26° it is already too concentrated, crystallizes too quickly, and yields too small crystals.

For dissolving, half mother liquor from refining and half condensed steam-water from the drying-plates are taken; the rest of the mother liquor is pumped back into the crude-salt pans; and thus an accumulation of impurities in these liquors is prevented. The dissolving takes place at a full boiling-heat. When the solution has got up to strength, it is allowed to settle for two hours, and, by gradually turning down the swivel pipe, is then run into one of the coolers. Having been already filtered by the canvas-covered drum, it is filtered a second time by a canvas bag suspended at the end of the leaded-out spout which conveys the hot liquor into the crystallizing-cones. The residue from dissolving is put back into the pans Q Q (figs. 164, 165), and thus again enters into the crude salt.

*The crystallizing-vessels (cones) for the finished salt* must be placed in a very clean special shed; its bottom, made of asphalt, stone flags, or some other tight material, should incline towards a catch-well, to save any thing spilt. The cones themselves are usually made of wood and lined with lead, with their bottoms boat-shaped or oval, or inclined to one side—all for facilitating the running-off of the mother liquors. The cones are made of pretty strong planks, in order to cool slowly and furnish large crystals. For the same purpose planed laths are put into the cones, upon which the finest crystals are found. The crystallization takes eight or nine days in winter, or fourteen days in summer. In the deepest part of each cone there is a plug-valve for running-off the mother liquor into a well, from which it is pumped, in part to the dissolver, in part back to the crude-liquor pans. The crystals are drained in the cones themselves, and again in canvas bags suspended in wooden frames or in lead-lined wooden drainers with false bottoms. They are washed with steam-water (from the drying-plate) till the chlorides are almost entirely removed. The most tenacious is the lead chloride; but this can always be kept out by adding in the dissolving a little (say  $\frac{1}{2}$  lb.) pure soda-ash, by which the lead and some lime are precipitated as carbonates, and also mechanically carry down any suspended flakes of ferric hydroxide. The removal of the lead can be effected even more completely by adding a small quantity of sodium sulphide. With proper treatment the chlorides in the

potassium chlorate can be got down to 0.05 per cent. When the evaporation and crystallization of the crude salt has been carried on in iron vessels, very little lead is contained in the chlorate; but the presence of some has been distinctly shown, *e. g.* by Hilger (Wagner's Jahresb. 1871, p. 446).

At Péchiney's works, the second crystallization is performed in very shallow (6-inch deep) leaden vessels, without any strips of wood or lead placed inside; by means of light wooden canvas-covered frames the cooling is prevented from being too rapid. No very large crystals can be thus obtained, but this does not matter there; on the contrary, it is found that the smaller crystals are more easily purified by centrifugalling and washing than larger ones, and a chemically pure product can be thus obtained. 1 cubic metre of liquor yields 250 to 300 kils. finished crystals.

The washed salt is *dried* on a hollow iron plate, like those used in calico-printing works, but placed horizontally and covered with lead. It is possible to dry upwards of 1 cwt. per square yard of surface in 12 hours. The drying-plates can be heated by the waste steam from dissolving, pumping, and grinding, direct steam from the boiler making up the deficiency. At the other end there is an automatic apparatus for discharging the condensed water without allowing any steam to escape. This water is collected in a well, which is lined with lead, and employed for washing the finished and dissolving the crude salt. Of course care must be taken that no crusts are left on the lead, by scraping it with a sharp piece of hard wood.

The crystals are now sifted through a sieve with 8 holes to the linear inch, or less, as required; the powder falling through is ground while still warm (when quite cold it is apt to cake together), in a small horizontal mill like a flour-mill, between granite stones, or "French burrs," to an impalpable powder, which it is best to drive, in a cylinder sieve with rotating brushes, through miller's gauze. The sifted flour is best dried another time, and is well cooled down before being packed. There is no danger in grinding if the admixture of organic substances (wood, straw, &c.) or iron (nails, &c.) is avoided, and if care is taken that the bearings do not get heated by running too long, especially the "eye" of the bottom stone (through which the spindle passes). If the latter precaution be neglected, an explosion may take place.

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the use of overalls for the workmen in the grinding-rooms, on account of clothing becoming impregnated with chlorate dust and catching fire, also the use of some such lubricant as tallow instead of oil, ventilating-cowls in the roof, electric lighting where practicable, and baths kept ready for use.

Jurisch (p. 44) states that at Muspratt's the "finishing-house" was constructed entirely of stone and iron, with iron frames for the roof and iron doors, rendered necessary on account of the danger from fire to which wood is exposed if covered with fine chlorate dust or soaked with chlorate liquor and then dried. In contrast to this commendable precaution, the crystallizing-cones, the staves for the crystals to grow on, the bogies for carrying the salt, &c. were all made of wood. Other finishing-houses are made of brickwork, with a stone floor, but with wooden doors and roofing-frames, without causing any harm. Of course there must be no fire either within or next to the finishing-house, and smoking &c. must be strictly prohibited. The heating is done by steam, the lighting by reflectors from without or by incandescent electric light. The mill ought to be in a separate fire-proof shed, to prevent any small explosions from setting fire to the finishing-house.

### *Yields and Costs.*

The *cost* of chlorate of potash will, of course, differ very much, according to whether the chlorine is made from native manganese ore or by the Weldon process. By Deacon's process also much chlorate is made; and this seems to be very appropriate, since the drying of the gas by sulphuric acid is unnecessary, and any contamination by carbonic acid does no harm.

It is generally assumed that 1 part of potassium chlorate requires  $6\frac{1}{2}$  times as much chlorine as 1 part of bleaching-powder; hence, with native manganese ore containing 70 per-cent.  $MnO_2$ , about 6 tons will be required for 1 ton of chlorate. The latter moreover requires 17 to 18 cwt. of good (90–95-per cent.) muriate of potash. Theoretically, only  $12\frac{1}{2}$  cwt. of pure  $KCl$  or  $13\frac{1}{2}$  cwt. of 90-per-cent. muriate are required; the remainder is lost, principally in the mother liquor—partly as such, partly as chlorate. Besides, about  $2\frac{1}{2}$  to 3 tons of lime and about 4 or 5 tons of coals are needed for evaporating, dissolving, and steam for the engines,

apart from the fuel required for manufacturing the chlorine. The amount of labour in proportion to the scale of the manufacture differs so much that no general statements can be made about it; it is pretty much the same whether 2 or 8 cwt. are turned out per diem. One man attends to the absorbers, another to the pans and the crystallization of the crude salt, a third and a boy to the refining and grinding; when more is made, one or two men are wanted for getting the lime &c.

According to experiments by F. Hobrecker (cited by Mylius in Hofmann's Bericht, 1875, i. p. 127, but without stating whether they were made on the large or the small scale), 100 parts of potassium chlorate require

4431.0	parts	hydrochloric acid of 32° Tw.
772.0	„	65-per-cent. manganese.
418.0	„	lime.
72.7	„	92-per-cent. potassium chloride.
2262.0	„	brown coal.

[Acid, manganese, coals, and lime are set down much too high, potassium chloride too low.]

Roscoe and Schorlemmer (Lehrbuch, ii. p. 58) give the quantities required for manufacturing 1 ton of chlorate of potash as follows—about 37 to 40 tons hydrochloric acid of sp. grav. 1.15, 16 to 20 cwt. of potassium chloride, 3 tons lime, 5½ tons 70-per-cent. manganese, and 10 to 12 tons of coal.

Jurisch (p. 144) states that 100 parts 90-per-cent. KCl, which ought to yield 148 KClO<sub>3</sub>, yield only 104.7 with the ordinary process (=70.8 per cent.), or 110.1 when utilizing the mother liquors described p. 527 (=74.4 per cent.). Generally it may be calculated that 100 parts potassium chlorate require 90 parts 90-per-cent. muriate of potash, of which 25 per cent. = 22½ parts by weight are lost in the mother liquors.

The consumption of *hydrochloric acid* is stated by Jurisch on p. 121 with the Weldon process = 35 tons acid of 28° to 30° Tw. per ton of chlorate; on p. 142 he gives 39½ tons; when employing mother-liquor gas only 29½ tons of 30° Tw. (p. 135), equal to 16 tons of 90-per-cent. common salt. With the Deacon process, employing the HCl recovered for the Weldon process and utilizing

the mother-liquor gas, the consumption of acid was only  $21\frac{1}{2}$  tons of 30° Tw. =  $11\frac{3}{4}$  tons 90-per-cent. salt. He assumes that 1 ton of chlorate requires  $7\frac{1}{2}$  times as much chlorine than 1 ton of 35-per-cent. bleaching-powder with the Weldon process, but only 4·7 to 5·85 times as much by the Deacon process. [For the exceedingly involved calculations upon which Jurisch founds the just-mentioned assertion, I must refer to the original. For the Weldon process his statement is rather less favourable than the usually assumed proportion 1 :  $6\frac{2}{3}$  or 1 : 7 ; for the Deacon process is it far more favourable than usually allowed.]

The consumption of *coals* is stated by Jurisch (p. 143) = 15 or 16 tons (with 10 to 15 per cent. ashes) for 1 ton of potassium chlorate, in comparison with 1 ton per ton of bleaching-powder by the Weldon, or 10 cwt. per ton of bleach by the Deacon process.

The following items are also from the same source (p. 147) :— The consumption of *manganese ore*, when employing the Weldon process and filter-pressing the mud (p. 339), does not exceed 5 cwt. per ton of chlorate. In the Deacon process the cost of copper and clay ranges from 20s. to 49s. per ton of chlorate (without wages).

The consumption of *quicklime* is from 2·2 to 3·1 tons, average 2·77 tons per ton of chlorate.

The consumption of water per ton of chlorate is at least 106 tons, 72 tons of which is consumed in the production of steam.

For the *total cost* of making chlorate of potash, Jurisch (p. 156 *et seq.*) gives extremely involved calculations, according to whether the Weldon or the Deacon process is employed. As, especially with respect to the latter, very much has been changed, in the first instance most of the prices, during the 15 years since Jurisch obtained his notes, we shall here only quote the quantities mentioned by him as required for manufacturing 100 kil. chlorate of potash by the Weldon process :—

A. For manufacturing the *chlorine* by the Weldon process, with utilization of mother liquors :

3000 kil. hydrochloric acid 32° Tw.

25 „ manganese ore.

520 „ quicklime.

260 „ limestone dust.

750 „ steam coals.

Wages about 5s.

**B. For manufacturing the *chlorate* itself:**

260 kil. quicklime.

90 „ muriate of potash 90 to 94 per cent.

1600 „ coals.

Wages about 6*s*.

When not employing the mother liquors for the production of chlorine, the cost is a little higher. By the Deacon process it is decidedly less. Jurisch quotes the cost = 56*s*. per 100 kil. by the Deacon process, against 62*s*. by the Weldon process; for Germany he estimates the cost by the Weldon process at 110*s*., by the Deacon process at 42*s*., evidently much too high for the first, and much too low for the second case. The absurdity of his calculations for the Deacon process has been demonstrated by Eschellmann (Chem. Ind. 1889, p. 54), who very justly points out that the Germans would not be so foolish as to import very large quantities if they could manufacture it for themselves at prices even remotely near those calculated by Jurisch on the basis of the most arbitrary assumptions [probably about one half of the actual cost]. Jurisch replied in the same publication 1890, p. 101, but was again refuted by Eschellmann on p. 102.

**THE MAGNESIA CHLORATE PROCESS.**

Weldon as early as 1871 (Engl. pat. 2389, 1871) proposed to replace the lime in the ordinary chlorate process by magnesia, to decompose the  $MgCl_2$  formed by heat, and to recover therefrom both magnesia and free KCl or Cl. This process was probably abandoned because the above-mentioned treatment of magnesium chloride, which had roused great expectations for the chlorine industry generally, presented greater difficulties than had been at first assumed. According to a later patent (No. 98, 1883) Weldon proposed to employ for the manufacture of chlorate magnesium hydrate, prepared by the action of magnesium chloride on calcium sulphhydrate, and to apply the  $MgCl_2$  formed over again for the same process, viz. Schaffner and Helbig's sulphur-recovery process from Leblanc waste, Vol. II. p. 857.

The magnesia process was taken up again by Muspratt and Eschellmann (Engl. pat. 3960, 5168, & 5183, 1883). Chlorine is passed into a milk of magnesia and water, until the conversion into magnesium chlorate and chloride is complete. Then potassium

chlorate is added, the liquor is boiled down and allowed to crystallize. The  $\text{MgCl}_2$  mother liquor is boiled down to dryness and the residue is decomposed by heat. (Up to this point the process is identical with Weldon's.) Or else the first liquor, *before* adding the potassium chlorate, is boiled down to between  $64^\circ$  and  $76^\circ$  Tw.; on cooling, magnesium chloride crystallizes out and 4 mols.  $\text{MgCl}_2$  remain to 1 mol.  $\text{MgCl}_2\text{O}_6$ . Now potassium chloride is added, and the potassium chlorate is allowed to crystallize out, from 5 to 10 per cent. of it remaining in the mother liquor. This is treated with hydrochloric acid and steam, to evolve chlorine from the chlorate; the excess of  $\text{HCl}$  is neutralized by magnesium carbonate, the liquor is boiled down to  $90^\circ$  Tw. and is cooled down. It solidifies to magnesium chloride, which is sold to cotton-spinners for sizing the yarn, or decomposed by heating to  $\text{MgO}$  and  $\text{HCl}$ . Or else the magnesia is precipitated by sodium carbonate or hydrate, or a mixture of both, and used over again. In the latter case the liquor is first boiled down to  $75^\circ$  or  $80^\circ$  Tw., and a little  $\text{MgCl}_2$  allowed to crystallize out. According to pat. No. 1900, 1885, the injurious action of magnesium chlorate or hypochlorite on the metal of the boiling-down pans (which would cause the magnesium chloride to be stained red by ferric oxide) is to be prevented by adding to the liquor magnesia, lime, soda, or a reducing agent, or by converting the magnesium chlorate into potassium or sodium chlorate.

The process as carried out by Messrs. Muspratt has been described in detail by Higgins (Journ. Soc. Chem. Ind. 1887, p. 248). The first material is Euboean magnesite, containing 93 to 97 per cent.  $\text{MgCO}_3$ , with 1.5 to 3.5 per cent.  $\text{CaCO}_3$ , and 1.5 to 4.2 per cent.  $\text{Fe}_2\text{O}_3$ , &c. It is more easily burned than limestone, 0.7 to 4.5 per cent. remaining in the product. Well-burnt magnesia is light, as soft as chalk, and often of columnar structure, like starch. When too much burnt, it is hard and dense and of no use for the chlorate process.

Later on (No. 2786, 1889) Muspratt and Eschellmann patented the use of precipitated magnesium hydrate, because  $\text{MgO}$  is not sufficiently active. The magnesia must be ground very fine and made with water into a milk, which is exposed to the treatment with chlorine. In this the liquor does not get so hot as with lime, viz., usually only  $43^\circ$ , or at most  $60^\circ$ , while similarly treated lime liquor gets much hotter [this is a complete refutation of the statements of



Jurisch, p. 513]. Even in the cold, near the freezing-point, the conversion into chlorate is complete [this entirely agrees with my results, p. 493]. The liquors show between  $40^{\circ}$  and  $50^{\circ}$  Tw. The pink colour in this case is not, as in that of lime, a sign of the completion of the process; it sets in already when very much magnesia is still left. The loss of oxygen is very slight; the proportion of chloride to chlorate approaches 5 : 1 and rarely exceeds 5.1 to 1, while with lime it varies between 5.3 to 5.6, and 5.4 is considered good work. [This evidently arises from the quicker transition of magnesia hypochlorite into chlorate.] Sometimes a very unpleasant incident occurs, viz., the changing of the liquor into a pasty mass, through the formation of magnesium oxychloride.

The finished liquor is now boiled down, in which process no magnesium chlorate is decomposed, and this is continued, until on cooling half of the magnesium chloride is separated as  $\text{MgCl}_2$ ,  $6\text{H}_2\text{O}$ ; the liquor now contains 2.8 mols.  $\text{MgCl}_2$  to 1 mol.  $\text{MgCl}_2\text{O}_6$ . It is not possible to go further, because otherwise the mass on cooling gets too hard and is not easily removed from the vessels. The magnesium chloride crystals are easily freed from the mother liquor; this is mixed with exactly the theoretical quantity of potassium chloride, taking care not to leave any of it undissolved, and by cooling the potassium chlorate is made to crystallize. Any excess of  $\text{KCl}$  would lead to the crystallization of carnallite,  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $6\text{H}_2\text{O}$ , and must be avoided for that reason, apart from the loss. The crude crystals of chlorate of potash have quite a different appearance from those obtained in the lime process, and they are much purer. Since potassium chlorate is less soluble in magnesium-chloride solution than in calcium-chloride solution, much less of it is lost in the mother liquor, and 90 per cent. of it can be separated by crystallization. While in the lime process the average left in the mother liquor is 30 grams  $\text{KClO}_3$  per litre, it is only 19 grams in the magnesia process, and even as little as 10 grams has been found. The finishing of the crude crystals takes place in the usual manner, and is very easily performed.

The mother liquor, together with a solution of the previously crystallized magnesium chloride, is run into a chlorine-still. Here, by means of hydrochloric acid and steam, all the chlorate is decomposed with evolution of chlorine, which is finished at  $60^{\circ}$  C. Care must be taken on account of explosions (p. 527). The

liquor, after driving out the chlorine, is neutralized by magnesia in an apparatus constructed without any iron parts; a certain quantity of a solution of magnesium sulphate (from kieserite) is run in, in order to precipitate the lime present as  $\text{CaSO}_4$ , and the liquor is settled in order to remove the calcium sulphate, ferric oxide, &c.

The purified magnesium-chloride liquor is boiled down in cast-iron pans (wrought-iron is too much acted upon). Here more calcium sulphate is always precipitated, and iron is dissolved, which cannot possibly be separated in the shape of protoxide, but only in that of peroxide. This is done by heating the liquor, just before finishing it, to strong boiling, oxidizing the iron (probably by bleaching-powder) and precipitating it by magnesia. After settling, the greenish liquid is ladled off into casks, where it solidifies. The product is solid magnesium chloride, with 47 per cent.  $\text{MgCl}_2$ , free from iron and  $\text{CaCl}_2$ .

We see from this description that the process of precipitating and re-employing the magnesia (p. 538) was not carried out. The only economical way of proceeding seems to be to manufacture crystallized magnesium chloride for cotton-sizing, and this, considering the competition from Stassfurt, seems to stand in the way of any extension of that process beyond local limits (compare, however, the new patent of 1889, p. 538, which deals with the reintroduction of the magnesium chloride into the process by precipitating magnesium hydrate).

In the nature of things, the magnesia-chlorate process should be especially adapted for such works where chlorine is made by one of the magnesia processes described in the next chapter, as by means of these ultimately the whole of the chlorine, not merely  $\frac{1}{6}$ , should be converted into chlorate. In fact, as early as 1871 this was Weldon's aim; but he was not in possession of a proper way for attaining it, nor can this task be considered as accomplished even at the present day.

According to Chem. Zeit. 1888, p. 1591, the Péchiney-Weldon process (comp. Chap. XXIII.) is applied to the manufacture of chlorates in the following way at Salindres. The chlorine is absorbed in a milk of magnesia and water, holding from 50 to 100 grams  $\text{MgO}$  per litre; this takes place with more difficulty than with lime. The liquid obtained after settling tests from  $32^\circ$  to  $40^\circ$  Tw.; it is boiled down to  $100^\circ$  Tw. (measured hot) and allowed to cool in iron vessels, most of the magnesium chloride

crystallizing out. The whole mass is crushed and centrifugalled, which causes most of the  $\text{MgCl}_2$  to be separated from the mother liquor. The latter is boiled down again and magnesia is added, to form insoluble magnesium oxychloride; this is again centrifugalled, and, as it contains some chlorate, it is used over again in the next operation. To the solution of magnesium chlorate, now tolerably pure, potassium chloride is added, with 5 to 10 per cent. excess over the theoretical quantity, the liquid is boiled down to  $74^\circ \text{Tw.}$  and allowed to crystallize. The mother liquors contain the excess of  $\text{KCl}$ , with a little  $\text{KClO}_3$  and  $\text{MgCl}_2$ . The whole of the magnesium chloride goes back into the Péchiney-Weldon process [which seems to have been discontinued at the same works some time ago].

Weldon (Engl. pat. 5975, 1884) proposes mixing magnesia with potassium chloride and treating the mixture with chlorine. [This cannot have done much good.]

Twynam (Engl. pat. 4397, 1881) proposes employing burned dolomite for the manufacture of potassium chlorate.

The *cost* of chlorate of potash, made by the magnesia process, is calculated by Eschellmann (Chem. Ind. 1889, p. 53) to amount to 522 mark = £26 per ton for Germany; but this is based on the assumption that the magnesium chloride can be used up for the Péchiney-Weldon process, which appears impracticable. His calculation has therefore no practical value.

#### *Manufacture of Potassium Chlorate by means of Zinc Oxide.*

Bayer (Engl. pat. 17978, 1894) employs zinc oxide, free from iron, manganese, and arsenic, made into mud with water and mixed with 1 mol.  $\text{KCl}$  to 3 mol.  $\text{ZnO}$ . Before passing in the chlorine the temperature is raised to  $95^\circ$  or  $98^\circ \text{C.}$ , in order to prevent the precipitation of zinc oxychloride and yet to bring as much  $\text{ZnO}$  into alkaline solution as possible. He states that it is converted directly into chlorate, without the intermediate stage of hypochlorite. The liquor is evaporated to spec. grav. 1.38, cooled down, the crystals of potassium chlorate are removed, the mother liquor is concentrated to spec. grav. 1.71, cooled down to  $0^\circ \text{C.}$ , the fresh crop of crystals is removed, and the last mother liquor is boiled down to spec. grav. 1.9 or upwards, in order to obtain solid  $\text{ZnCl}_2$ ; or else it is first heated with hydrochloric acid, to decompose the chlorate still present, utilizing the chlorine. In the Chem.

Zeit. 1895, p. 1453, Bayer recommends his process as very rational, without, however, adducing any proof for this from practical experience.

### *Commercial Chlorate of Potash.*

Chlorate is usually packed in hundredweight casks laid out with blue paper. Powder and crystals fetch the same price. In regular work about 2 or 3 parts of crystals are obtained to 1 part of powder. The latter ought to be of a snow-white colour and as fine as flour, without any grittiness. The crystals ought to be pretty large plates, thin, brilliant and transparent, not porcelain-like; the latter may easily occur from excessive drying.

The *examination* of chlorate of potash is usually done by dissolving a large quantity (by which a perfectly clear solution must be produced, as any impurities, especially of an organic nature, may cause very unpleasant consequences in using the chlorate) and testing for chlorides by silver nitrate. Iron or lead would be detected by ammonium sulphide.

The percentage of chlorides is usually calculated as  $\text{CaCl}_2$ , and ought not to exceed 0.05 per cent.; according to Jurisch since 1876 the limit is 0.04 per cent. He states the average composition of crystals = 99.77 per cent.  $\text{KClO}_3$ , 0.03  $\text{CaCl}_2$ , 0.20  $\text{H}_2\text{O}$ ; of powder = 99.82 per cent.  $\text{KClO}_3$ , 0.03  $\text{CaCl}_2$ , 0.15  $\text{H}_2\text{O}$ .

Garnier (Fischer's Jahresb. 1885, p. 260) has sometimes found arsenic in chlorate of potash.

Nitrate of potash is sought for by Buchner (*cod. loco*) by placing 1 gram into a test-tube, adding a little iron filings and zinc dust, then caustic-potash solution, stopping the mouth of the tube with cotton-wool and covering it with turmeric-paper. A strong evolution of gas sets in; in the presence of  $\frac{1}{2}$  or 1 per cent. nitrate the turmeric-paper turns brown in a few minutes.

*Applications of Chlorates.*—Chlorate of potash is principally employed in the manufacture of lucifer matches (safety matches), for pyrotechnical purposes, and sometimes for explosives. Its use for the latter purpose is, however, greatly restricted by the dangerous properties of all explosives prepared with that reagent. Also as an oxidizing agent in dyeing and calico-printing, where it has been partially replaced by chlorate of soda, owing to the greater solubility of the latter. Further, in the manufacture of alizarine and for oxidations in some other industrial branches;

but mostly it is too expensive. It is used in laboratories for preparing oxygen—and in medicine, especially for gargling in cases of inflammation of the throat, &c.; but large quantities have a poisonous action, similar to other potassium salts.

*Statistical.*

Jurisch (p. 219) states that in 1887 there were ten works in Great Britain producing 5500 tons chlorate of potash per annum (Fletcher's estimates, made in 1887, amounting to 7000 tons, is probably too high). To this 100 tons of chlorate of soda should be added. In France there were two works, turning out 500 tons of chlorate of potash and 100 tons chlorate of soda; in Austria one, making 450 tons; in Germany three, making 300 tons. Total 6750 tons of potassium and 200 tons of sodium chlorate.

Since that time the state of affairs has been considerably changed by the introduction of electrolysis, which will be explained when dealing with that subject.

Korda (Monit. scient. 1894, p. 504) estimates the total production in 1894 at 8000 tons, of which 5000 were made in England.

Jurisch (p. 224) gives a table of selling prices. In 1867 the ton of chlorate of potash in Germany cost £125; but after that year, except in 1872 and 1873, the price constantly declined, and in 1885 had diminished to £49, since which it has been a little raised by a combination of the makers. In England the price has been about 5*d.* per lb. Chlorate of soda was for some time sold at fancy prices; but from 1879, when its manufacture on a larger scale was introduced, its price has been almost steadily £70 per ton.

CHLORATE OF SODA.

As this salt, owing to its solubility far exceeding that of the potassium salt, has since 1877 largely come into use, especially for aniline black in calico-printing, we shall briefly treat of its properties and preparation. It forms colourless crystals of the regular system, frequently plate-shaped. They present peculiar hemihedral faces and corresponding phenomena of circular polarization, pointed out by Marbach (Poggend. Annual. xci. p. 482, xciv. p. 412, xcix. p. 451). The salt is stable in the air; when heated it fuses and yields perchlorate, without evolving much oxygen.

Spec. grav. = 2.289. According to Kremers (ib. xcvi. p. 4) 100 parts of water dissolve

at 0° 20° 40° 60° 80° 100° 120° C.

81.9 99 123.5 147.1 175.6 232.6 333.3 parts NaClO<sub>3</sub>.

The boiling-point of the saturated solution is at 132°.

The specific gravities of solutions at 19.5° C. are,

for 10 15 20 25 30 35 per cent. NaClO<sub>3</sub>.

1.070 1.108 1.147 1.190 1.235 1.282

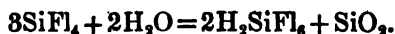
It dissolves at 16° in 34 times its volume of alcohol of 83 per cent., and less amounts of alcohol at higher temperatures.

According to Schloesing (Compt. Rend. lxxiii. p. 1272) sodium chloride influences the solubility of sodium chlorate thus: 100 parts of water at 12° dissolve 89.8 NaClO<sub>3</sub> or 35.77 NaCl; but when both salts are present in excess, 50.75 NaClO<sub>3</sub> and 24.4 NaCl are dissolved. At 122° C. 100 parts of water dissolve 249.6 NaClO<sub>3</sub> and 11.5 NaCl; and on cooling down to 12° C. they retain 68.6 NaClO<sub>3</sub> and all the NaCl (11.5). This behaviour is noticeable with regard to the preparation of the salt.

Chlorate of soda was formerly made from chlorate of potash, usually by means of hydrofluosilicic acid, first employed by Wheeler in 1817. One way of doing this is, decomposing chlorate of potash by hydrofluosilicic acid, separating the solution of chloric acid formed from the precipitated potassium fluosilicate, and saturating the chloric acid by soda; the solution of sodium chlorate is evaporated and cooled down for crystallization.

Or else the hydrofluosilicic acid is saturated with soda and the solution of sodium fluosilicate boiled with potassium chlorate, whereby a solution of sodium chlorate is formed directly. The hydrofluosilicic acid might be regenerated from the potassium fluosilicate by heating it with sulphuric acid and passing the evolved mixture of silicon tetrafluoride and hydrofluoric acid into water.

Hydrofluosilicic acid is made by heating a mixture of fluorspar, sand, and concentrated sulphuric acid in a cast-iron retort, and passing the silicon tetrafluoride into water, where it decomposes into hydrofluosilicic acid and silica:



The gelatinous silica might give some trouble by stopping up

the gas-pipe, &c.; but this can be prevented in various ways—for instance by passing the silicon tetrafluoride gas, not through a column of water, but through a channel in which it comes into contact with constantly moistened surfaces, such as a tower loosely packed with bricks. In a German patent (No. 9072, May 30, 1879) Zenisek and Schmidt describe an apparatus for this purpose. The silicon tetrafluoride, given off in a long cast-iron retort, is absorbed by water contained in a vessel provided with an agitator, which constantly breaks up the silica separating on the top of the water, and thus offers always a fresh surface of water to the action of the gas.

Wittstein (Rep. Pharm. xxxviii. p. 43) first suggested the conversion of potassium chlorate into ammonium chlorate, by evaporating it with ammonium sulphate and extracting the residue with alcohol; the alcoholic solution is freed from alcohol by boiling, sodium carbonate is added, and by further boiling ammonium carbonate escapes and sodium chlorate remains behind. [This process is probably too expensive, as loss of alcohol and ammonia cannot be avoided.]

Bottomley and Molesworth (Engl. pat. 3005, 1881) propose manufacturing sodium chlorate from potassium chlorate by means of sodium bitartrate. This method, prescribed several times before (by Hopper, Orme, Wittstein, and Winckler), is much too expensive.

As early as 1817 it was proposed to precipitate the potash in the chlorate by means of aluminium sulphate, in the shape of alum. This process was taken up by Schlumberger in 1872. He adds to a hot solution of 100  $\text{KClO}_3$  in 250 water, 362 aluminium sulphate dissolved in 181 water, and stirs till the mass is cooled down. The solution of aluminium chlorate, separated from the alum, is decomposed by sodium carbonate into alumina and sodium chlorate. [This process is hardly practicable on a large scale, as aluminium chlorate strongly acts upon all metals; apart from this, the reactions are imperfect, the losses are great, and the product is very impure.]

The direct preparation of sodium chlorate by the same process as potassium chlorate—that is, decomposing calcium chlorate by sodium chloride into 2 mols.  $\text{NaClO}_3$  and 5 (practically at least  $5\frac{1}{2}$ ) mols.  $\text{CaCl}_2$ —is not practicable, because the difference of solubility between  $\text{NaClO}_3$  and  $\text{CaCl}_2$  is too slight for effecting their separation. Economically impossible is Muck's proposal (Germ. pat. 25785) to pass chlorine into a solution of sodium carbonate and

hydrate, boil down to dryness, and extract the residue with hot saturated solution of sodium chloride, which is supposed to dissolve nothing but sodium chlorate. The treatment of the crude calcium-chlorate liquor with enough sodium carbonate to precipitate all the calcium existing as chlorate and chloride had been previously tried, but found too dear, and the separation of  $\text{NaClO}_3$  from  $5\frac{1}{2}$  or 6 mols.  $\text{NaCl}$  is too difficult.

The direct manufacture of chlorate of soda on the large scale was first effected by Péchiney's process (Engl. pat. 422 to 425, 1881). The ordinary chlorate liquor, prepared with lime and chlorine, is strongly concentrated in iron pans, without adding any potassium chloride, till  $100^\circ \text{Tw.}$  is reached, and is then cooled down not below  $10^\circ$  and not above  $12^\circ \text{C.}$  Four-fifths of the  $\text{CaCl}_2$  now crystallize out; the mother liquor, which is almost entirely soaked up by the crystalline mass, tests  $119^\circ \text{Tw.}$ , and contains per litre 480 grams = 1.2 mol.  $\text{CaCl}_2$  to 664 grams = 1 mol.  $\text{CaCl}_2\text{O}_6$ . The patent prescribes adding for each mol.  $\text{CaCl}_2$ , 3 mols.  $\text{CaO}$  in the shape of powder, with a little water, heating to  $80^\circ$ , and allowing the calcium oxychloride to separate by cooling; the solution now contains only 0.3 mol.  $\text{CaCl}_2$  to 1  $\text{CaCl}_2\text{O}_6$ , and is either converted into potassium chlorate, by adding  $\text{KCl}$  (which does not seem to have been done in actual work), or into sodium chlorate, by adding  $\text{Na}_2\text{SO}_4$  and sufficient  $\text{Na}_2\text{CO}_3$  to decompose the  $\text{CaSO}_4$  not precipitated. On evaporating the solution,  $\text{NaCl}$  is separated in the hot liquor and is removed by fishing-out; the mother liquor on cooling yields sodium chlorate. The fished sodium chloride is freed from chlorate by washing. The calcium oxychloride, which of course retains much chlorate, is mixed with fresh milk of lime and again converted into chlorate by treating with chlorine (comp. Weldon, Journ. Soc. Chem. Ind. 1882, p. 40).

Jurisch opines that this process would involve enormous mechanical and chemical losses, and must have been quickly abandoned. But, as I have reported in Chem. Ind. 1888, p. 225, I saw it in full work at Salindres in 1883; all the chlorate of soda turned out by that works, about 100 tons per annum, was then, and is probably even now, made by that process. Only the formation of oxychloride has been left out: the solution containing 1.2 mol.  $\text{CaCl}_2$  to 1  $\text{CaCl}_2\text{O}_6$  is employed directly, by adding sodium sulphate as long as any calcium sulphate is precipitated; the oxychloride process is only applied when making chlorate of baryta. If the



concentration and temperature are properly chosen, the calcium sulphate is precipitated in a crystalline form and can be almost completely freed from chlorate by washing. The  $\text{CaSO}_4$  still remaining in solution is precipitated by sodium carbonate; the filtered liquid contains nothing but  $\text{NaCl}$  and  $\text{NaClO}_3$ .

For separating these two salts the fact is made use of that a cold saturated solution of both salts together at  $12^\circ \text{C}$ . holds 50.75 grams  $\text{NaClO}_3$  and 24.40 grams  $\text{NaCl}$  in 100 c. c., but a solution saturated in boiling, at  $122^\circ \text{C}$ ., holds 249.6 grams  $\text{NaClO}_3$  and 11.50 grams  $\text{NaCl}$ ; on cooling the latter to  $12^\circ$  the whole of the  $\text{NaCl}$  with only 58.6 grams  $\text{NaClO}_3$  remains in solution, and 181 grams  $\text{NaClO}_3$  must crystallize out. The solution made as above is evaporated in steam-jacketed pans, the  $\text{NaCl}$  crystallizing out is fished out and washed free from chlorate, and the concentration is continued to  $100^\circ \text{Tw.}$ , whereupon the liquor is run into lead-lined coolers. The crystallization yields about 175 kil. sodium chlorate from 1000 litres; the mother liquor, which contains much chlorate, is added to the liquor obtained in a subsequent operation and concentrated again.

The first crystals still contain 1.5 per cent.  $\text{NaCl}$ , which is removed by a second crystallization. The second crystals are treated just like the potassium salt (p. 533) and thus go into the trade.

Weldon (Engl. pat. 424, 1881) suggested decomposing the crude chlorate liquor, made from lime and chlorine, directly with sodium sulphate into  $\text{CaSO}_4$  and a solution of sodium chlorate and chloride. This process does not seem to have been practicable; but a very similar one was later on proposed by Péchiney (Engl. pat. 16460, 1890)—the action of chlorine on a mixture of milk of lime with the equivalent quantity of *solid* sodium sulphate; this is to produce a much more concentrated liquor. Exactly similar to this is Nieske's patent, No. 10053, 1893.

At Widnes they manufacture sodium chlorate by Muspratt and Eschellmann's process (Engl. pat. 5183, 1883; comp. Jurisch p. 214). Chlorine is passed into a milk of magnesia and water (p. 537), whereby a mixture of 1 mol.  $\text{MgCl}_2\text{O}_6$  and 5.2 mols.  $\text{MgCl}_2$  is produced. This is sufficiently evaporated, and the greater part of the  $\text{MgCl}_2$  removed by crystallization, so that only 2.8 mols.  $\text{MgCl}_2$  remains. From this (or from the crude) liquor, the  $\text{MgO}$  is precipitated by sodium carbonate or hydrate, and the filtered solution

of  $\text{NaCl}$  and  $\text{NaClO}_3$  is boiled down to  $100^\circ$  or  $101^\circ \text{Tw.}$ , fishing out the  $\text{NaCl}$ ; on cooling the sodium chlorate crystallizes. The precipitated magnesia is converted into chlorate in a new operation.

Bolton, Wyld, and Auer (Engl. pat. 8217, 1887, and 10193, 1888) obtain sodium chlorate as a by-product in the manufacture of permanganate from manganate by chlorine.

Best and Brock (Engl. pat. 19189, 1894) manufacture chlorate of soda by passing chlorine into solutions of carbonate or bicarbonate of soda. The solution of  $\text{Na}_2\text{CO}_3$  is made of spec. grav. 1.27, and is saturated with chlorine at a temperature not exceeding  $37^\circ \text{C.}$  The evolution of  $\text{CO}_2$  taking place prevents a rapid rise of the temperature. The hypochlorous acid carried away with the  $\text{CO}_2$ , together with the excess of chlorine, are absorbed in separate vessels charged with sodium-carbonate solution. The chlorine is best pumped through the solution by means of the method described in patent 16151, 1893. The solution obtained (which is already very concentrated) is evaporated, the  $\text{NaCl}$  separates and is removed, and the  $\text{NaClO}_3$  is subsequently obtained by crystallization.

#### CHLORATE OF BARYTA.

This salt was obtained in 1814 by Gay-Lussac on treating caustic baryta with chlorine; but this is no commercial process. It crystallizes in fine, colourless, clinorhombic crystals, containing 1 mol.  $\text{H}_2\text{O}$ , and composed of 47.56 per cent.  $\text{BaO}$ , 46.85 per cent.  $\text{Cl}_2\text{O}_3$ , and 5.60 per cent.  $\text{H}_2\text{O}$ . The water is expelled at  $120^\circ$ . Spec. grav. = 2.988. 100 parts of water dissolve at  $0^\circ$ , 22.8; at  $20^\circ$ , 57; at  $100^\circ$ , 126.4 parts; boiling-point of the saturated solution,  $111^\circ \text{C.}$  Almost insoluble in absolute alcohol. Barium chlorate fuses at  $400^\circ$ ; already at  $250^\circ$  it yields oxygen, and in the presence of organic substances it is much less stable than potassium chlorate, so that in drying it explosions may be caused by dust, &c.

Barium chlorate may be prepared from an alcoholic solution of sodium chlorate by adding tartaric acid; the sodium tartrate is almost insoluble in the alcohol, and we obtain an alcoholic solution of chloric acid, from which barium chlorate can be obtained by means of barium carbonate (Duflos). A little cheaper is the treatment of an aqueous solution of sodium chlorate by oxalic acid; on artificial cooling by a freezing-mixture, sodium oxalate crystallizes out and chloric acid remains in solution (Böttger).

Apart from the expense, neither of these methods yields a product free from soda, which makes it useless for its principal application, viz. for green fire in pyrotechnical preparations. The only method formerly employed in actual practice was exactly the same as that at one time used for sodium chlorate, viz. decomposing potassium chlorate by hydrofluosilicic acid and neutralizing the free chloric acid thus obtained by barium carbonate. I saw this carried out on a manufacturing scale in 1864.

It is, however, cheaper to go by Péchiney's process: concentrating the crude chlorate liquor, made with lime and chlorine, till the greater part of the  $\text{CaCl}_2$  can be separated by crystallization, and only 1.2  $\text{CaCl}_2$  remains with 1  $\text{CaCl}_2\text{O}_6$  (p. 546). To this exactly 1 mol.  $\text{BaCl}_2$  is added; on cooling, barium chlorate crystallizes out, and calcium chloride remains in solution:



It is best to prepare a saturated boiling solution of barium chloride, and gradually add to it the proper quantity of concentrated chlorate liquor, previously separated from the calcium chloride. The crystals formed on cooling contain about 10 per cent.  $\text{BaCl}_2$ ; the mother liquor contains next to no Ba, but some  $\text{CaCl}_2\text{O}_6$ , and returns into the manufacture of potassium chlorate. By recrystallizing pure barium chlorate is obtained; the mother liquor, which contains much  $\text{BaCl}_2$ , is again employed for treating concentrated chlorate liquor.

Apart from pyrotechnical purposes, chlorate of baryta is employed in tissue-printing; some lakes are better obtained with the chlorate of barium than with that of potassium or sodium. It is also by far the best starting-point for the manufacture of free chloric acid or of any other chlorates, by adding to it the exact proportion of sulphuric acid or of the sulphate of the base in question.

## CHAPTER XXIII.

## OTHER PROCESSES FOR THE MANUFACTURE OF CHLORINE.

THE number of processes for manufacturing chlorine in other ways than those hitherto described, and everywhere employed in actual practice, is exceedingly large. We cannot be surprised at this, if we consider that formerly chlorine was only made by means of an intermediary, manganese ore, which was both costly and at that time found only in a very few localities. Later on, after Weldon's process had reduced the consumption of native manganese ore to a minimum, the drawback remained that only the minor portion of the chlorine of hydrochloric acid could be obtained in the free state. A further impetus for inventing new chlorine processes was the fact that the ammonia-soda process does not yield any hydrochloric acid.

The most important class of the new chlorine processes, those founded on electrolysis, will be treated in the last section. The other classes may be grouped as follows:—

- I. Chlorine from hydrochloric acid, made by other processes than the usual ones.
- II. Chlorine from common salt without converting it into HCl.
- III. Chlorine from calcium chloride.
- IV. Chlorine from magnesium chloride.
- V. Chlorine from ammonium chloride.

I. CHLORINE FROM HYDROCHLORIC ACID, MADE BY OTHER PROCESSES THAN THE USUAL ONES.

In this section we include all processes by which first of all HCl is liberated from common salt or other chlorides, and afterwards the hydrogen is abstracted from the HCl, either with or without previous condensation to liquid hydrochloric acid, by other means than those previously described and hitherto exclusively employed in actual manufacturing practice. We also include the

processes which start with mixtures of chlorides and sulphuric acid ; also those referring to manganese chloride, which must have been first prepared with free hydrochloric acid.

*Chlorine from various Metallic Chlorides by means of Manganese Peroxide and Sulphuric Acid.*

Binks (Engl. pat. 1319, 1853) prepares chlorine by heating the chlorides of manganese, iron, zinc, calcium, or aluminium with peroxide of manganese and sulphuric acid, in which case of course the HCl liberated from the chlorides acts upon the  $\text{MnO}_2$ . This process, evidently useless at that time, received only provisional protection.

In several modern processes the starting point is the treatment of manganese-sulphate liquors, formerly run to waste, in such manner that the manganese is re-converted into  $\text{MnO}_2$ , and also the sulphuric acid is in some way utilized.

Dormer (Engl. pat. 5225, 1889 ; comp. p. 287) decomposes  $\text{MnO}_2$  with NaCl and sulphuric acid, treats the manganese-sulphate solution with  $\text{CaCl}_2$  to produce  $\text{CaSO}_4$  and  $\text{MnCl}_2$ , and recovers from the latter  $\text{MnO}_2$  in the usual manner.

Mactear (Engl. pat. 10813, 1884) mixes the solution of  $\text{MnSO}_4$  with  $\text{MgCl}_2$ , boils down in the absence of air, condensing the HCl given off, and separates in the residue the magnesium sulphate from manganese oxide by lixiviation. The manganese oxide can then be further oxidized [in what way?] to produce chlorine.

Steedman and Kirkpatrick (Engl. pat. 18921, 1888 ; 889, 1889) boil the  $\text{MnSO}_4$  solution with magnesium carbonate (or  $\text{MgCl}_2$  and  $\text{CO}_2$ ), or with ammonium carbonate ; manganous carbonate is precipitated and magnesium sulphate is dissolved. The  $\text{MnCO}_3$  is filtered, washed, and converted into  $\text{MnO}_2$  by heating with air (p. 321). The solution of  $\text{MgSO}_4$  is dried down, and the residue heated with NaCl ; HCl escapes and the residue consists of  $\text{Na}_2\text{SO}_4$  and  $\text{MgO}$ , which is obtained by washing out the  $\text{Na}_2\text{SO}_4$ . When employing ammonium carbonate, the liquor is heated and the  $\text{NH}_3$  recovered ; the residue consists of a solution of sodium bisulphate, which is employed for decomposing NaCl in the first operation.

Albright and Hood (Engl. pat. 9271, 1893) produce manganous sulphate by heating manganese ore with coal-dust and

sulphuric acid, or in some other way, and treat it with calcium chloride (comp. Dormer's process, pp. 287 and 551) or with ammonia, in order to submit it to the Weldon process.

Campbell and Boyd (Engl. pat. 3407, 1889) begin also with converting  $\text{MnSO}_4$  by  $\text{CaCl}_2$  into  $\text{CaSO}_4$  and  $\text{MnCl}_2$ . 60 to 70 per cent. of the solution of manganous chloride is to be mixed with neutralized still-liquor and to be worked for  $\text{MnO}_2$  by the Weldon or Dunlop process. The remaining 30 or 40 per cent.  $\text{MnCl}_2$  are boiled down to spec. grav. 1.3 or 1.35, mixed with an equivalent quantity of Weldon mud which has been freed from  $\text{CaCl}_2$  by washing, and treated with sulphuric acid. Nearly all the chlorine is liberated; the Mn is converted into sulphate, which is neutralized with washed Weldon mud and after settling is decomposed by  $\text{CaCl}_2$  as above.—For the above-mentioned object the Weldon (or Dunlop) mud must be purified from lime as much as possible, by treating it with enough hydrochloric acid to dissolve the lime; the chlorine produced is expelled, and the  $\text{CaCl}_2$  liquor used as above; or else the lime of the mud is decomposed by  $\text{MnCl}_2$ . [The object of this and previous patents of the same inventors is, of course, to liberate the total chlorine from  $\text{HCl}$ . They must, however, for this purpose employ sulphuric acid, equivalent to  $\frac{1}{2}$  of the chlorine, and this acid reappears as calcium sulphate. They propose to utilize this as "pearl hardening" (Vol. II. p. 721); but this is impracticable, both on account of the insufficient purity and the limited sale of the product.]

In 'Industries,' xiii. p. 66, some details of the working of Campbell and Boyd's process are given. Instead of water, the  $\text{HCl}$  is absorbed by still-liquor. The acid solution of  $\text{MnCl}_2$  is heated with  $\text{MnO}_2$  and this is repeated until a very concentrated solution of  $\text{MnCl}_2$  has been formed, which is boiled down to dryness. The dry  $\text{MnCl}_2$  is decomposed with sulphuric acid, exactly like common salt, in an ordinary saltcake-furnace; the operation goes on much more quickly and at a lower temperature than with common salt.—According to the other process the  $\text{MnCl}_2$  liquor is mixed with  $\text{MnO}_2$ , the mixture is treated with sulphuric acid in a saltcake furnace, and the chlorine is utilized. In both cases ultimately  $\text{MnSO}_4$  is obtained which, if not heated too little, is devoid of chloride or free  $\text{HCl}$ . This sulphate is now converted into carbonate. It is dissolved for this object in water or weak ammonium sulphate solution, neutralized with gas liquor, if needful,

and settled. The clear liquor is run through three or more pans, provided with agitating-gear, in which it meets the gases from a gas-liquor still, containing mostly ammonium carbonate and sulphide; at the same time lime-kiln gases are passed through. The  $\text{NH}_3$  is completely absorbed and converted into sulphate; the manganese is converted into carbonate; the excess of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  escape and are utilized in some shape. The mass, when finished in any one of the pans, is neutralized with manganous sulphate solution and filter-pressed. The solution coming from the press is worked for pure ammonium sulphate; the  $\text{MnCO}_3$  is converted into 80–85 per cent.  $\text{MnO}_2$  by Dunlop's process.

Later on (Engl. pat. 12426, 1893; comp. also p. 322) Campbell and Boyd mix the solution of manganous sulphate with equivalent quantities of sodium-carbonate solution, separate the  $\text{MnCO}_3$  from the solution of  $\text{Na}_2\text{SO}_4$  and convert it into  $\text{MnO}_2$  by Dunlop's process (p. 321). Or else they run the solution of  $\text{MnSO}_4$  slowly, in a Weldon oxidizer, into a solution of caustic soda and oxidize the mixture by air, whereupon they separate the  $\text{Na}_2\text{SO}_4$  from the recovered  $\text{MnO}_2$ .

*Chlorine by Permanganates.*—Condy obtained provisional protection (No. 3411, 1866) for the evolution of chlorine from a mixture of common salt, sodium permanganate, and sulphuric acid; the latter was gradually to be added to the mixture. This process was to be employed chiefly for disinfecting, but also for manufacturing-purposes when quite pure chlorine was required. Comp. also the patent of De Sussex, No. 11585, 1847 (in the section "magnesium chloride"). Balmain (No. 1059, 1869) adds nothing novel.

Later on Tessié du Motay took up the employment of permanganates for the manufacture of chlorine (Wagner's Jahresb. 1871, p. 255; 1873, p. 270). He passes a current of  $\text{HCl}$  into a dark-red-hot retort filled with a mixture of manganese peroxide and lime.  $\text{Cl}$  and  $\text{H}_2\text{O}$  escape;  $\text{MnO}$  and  $\text{CaCl}_2$  remain behind. The chlorine is utilized in the ordinary way; over the residue a current of air is passed at the same temperature as before; thus the chlorine contained in the  $\text{CaCl}_2$  or  $\text{MnCl}_2$  becomes free and escapes, mixed with  $\text{N}$  and air in excess. The gases are passed into receivers containing a mixture of  $\text{CaO}$  and  $\text{MnO}$  (made by decomposing  $\text{MnCl}_2$  with an excess of lime); here hydrated  $\text{MnO}_2$ , bleaching-powder, and  $\text{CaCl}_2$  are formed. This mixture is treated

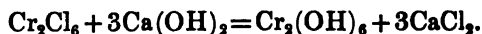
with HCl in the usual way, and the evolved chlorine passed into bleach-chambers. In the receivers a mixture of  $\text{MnCl}_2$  and  $\text{CaCl}_2$  remains behind, which is treated with lime, and this is again converted into a mixture of  $\text{MnO}$  and  $\text{CaO}$  (both hydrated). The  $\text{CaCl}_2$  yielded in the different operations is treated with magnesium carbonate, and the  $\text{MgCl}_2$  heated so as to obtain HCl from it. The inventor asserts that, 1st, the manganese oxides are continually regenerated; 2nd, all the chlorine of the hydrochloric acid is obtained; and, 3rd, all the chlorine is obtained in a pure state.

Cosnett, Bonnison, and Hayes (pat. No. 5849, 1893) propose making chlorine from the calcium-chloride liquor of the ammonia-soda process by sulphuric acid and potassium permanganate, and to manufacture bleaching-powder in that manner!

*Chlorine from Chromates and Hydrochloric Acid.*—MacDougal and Rawson (No. 12333, 1848) patented the manufacture of chlorine by heating chromates or bichromates, preferably those of calcium, with hydrochloric acid, either in the free or the nascent state. The residue of mixed chlorides and chromium salt is treated with nitric acid, the HCl distilled off, and the residue heated further; the chromate is thus regenerated, and nitrous gases are evolved, from which nitric acid is recovered by the action of air and water. Peligot (Ann. Chim. Phys. [2] lii. p. 267) and Gentile (Dingl. Journ. cxxv. p. 492) recommended this process. They employed the compound  $2\text{KCl} \cdot \text{Cr}_2\text{O}_6$ , discovered by Peligot, which on heating to  $100^\circ$  gives off its chlorine almost entirely (Wagner's Jahresb. 1861, p. 177). The application of calcium chromate was patented by Shanks (No. 2018, 1858), with the addition of recovering the chromates in a cheaper way. Starting from calcium chromate and hydrochloric acid, there are formed calcium chloride, chromic chloride, water, and chlorine, thus:



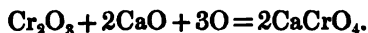
Half of the chlorine escapes in the cold, the other half is driven off by heating; this can be done in the ordinary chlorine-stills. The green solution is neutralized with lime, and by more lime all chromium precipitated as hydroxide:



Another two molecules of calcium hydrate are added, and the



precipitate collected on a filter ; the solution of  $\text{CaCl}_2$  runs away ; and the mixture of chromium oxide and lime is calcined in a reverberatory furnace at a dark-red heat with excess of air ; oxygen is absorbed, and calcium chromate regenerated, thus :



The chromium oxide thus acts as carrier between the atmospheric oxygen and the hydrogen of  $\text{HCl}$  ; in this way the manganese ore was to be entirely done away with. But theoretically from 16 molecules of  $\text{HCl}$  only 6 atoms chlorine are obtained, whilst by means of  $\text{MnO}_2$ , 8 atoms  $\text{Cl}$  would be got ; the excess of  $\text{HCl}$  practically required is no less in the first case than in the second. This is the first great drawback ; but it is very doubtful whether the cost of precipitation by lime, filtering, and calcining does not exceed that of fresh manganese ore ; and in no case can a competition with the Weldon process be thought of. In fact Shanks's process, after working a short time, was given up again.

Another process for the recovery of the chromates was proposed by Claus (pat. No. 1054, 1867). The mixed solutions of calcium and chromium are evaporated to dryness in a reverberatory furnace with a brick hearth, and the residuary mass is heated with admission of air at a temperature somewhat below the fusing-point of calcium chloride—say, between the melting-points of lead and zinc. Thus calcium chromate is recovered and hydrochloric acid and chlorine escape mixed with other gases. The hydrochloric acid is washed out in a coke-tower ; and the chlorine is retained in another tower by a stream of water holding hydrated lime or magnesia in suspension. The hypochlorites thus formed are utilized for generating chlorine by means of hydrochloric acid, or, less advantageously, for converting chromium chloride into chromate. If magnesia be employed, the magnesium chloride formed is decomposed by heat into hydrochloric acid and magnesia. The most obvious difficulties of this process are the evaporation of the acid liquors in a brick furnace and the complete conversion of the chromium chloride into chromate.

Fitzgerald (pat. No. 5542, 1886, and 5995, 1889) proposes regenerating chromic acid from the solution of chromic oxide by electrolysis.

Mond and Hargreaves (prov. prot. No. 1312, 1870) pass  $\text{HCl}$  with air over magnesium chromate, &c.

*Chlorine from Red Lead and Hydrochloric Acid.*—Robinson (prov. prot. No. 88, 1860) produces chlorine by treating red lead with hydrochloric acid; the  $\text{PbCl}_2$  is to be converted into  $\text{PbCO}_3$  by the solution of a carbonate (preferably that of ammonium), and the lead carbonate to be utilized as such or converted into red lead by heating. [This process is useless for many reasons. By the reaction  $\text{Pb}_3\text{O}_4 + 8\text{HCl} = 3\text{PbCl}_2 + 4\text{H}_2\text{O}$  only a quarter of the chlorine is transformed into the free state, even by theory. Further drawbacks are the high price of lead, its great atomic weight, the difficult and expensive reconversion into red lead, &c. Even as a white-lead process it would be too expensive.]

*Chlorine from HCl by Atmospheric Air.*—These processes are partly predecessors of the Deacon process (p. 371 *et seq.*). The first of them was patented by Oxland (No. 10528, 1840); the mixture of the two gases is passed through red-hot pumice, then cooled, and the unchanged HCl washed out by water.

Jullion (patent No. 11425, 1846) passes HCl and oxygen gas through heated platinum sponge, and washes the chlorine gas with water. Binks (prov. prot. No. 1563, 1860) decomposes HCl by atmospheric oxygen at a high temperature in the presence of a substance retaining the water but not the chlorine. In 1862 (No. 1496) he again applied for a patent for the same thing, adding to it the employment of concentrated sulphuric acid; and once more (No. 3085, 1862), without any essential novelty. Sequeville obtained provisional protection (No. 1831, 1865) for obtaining chlorine by passing dry HCl and air over red-hot pumice; inversely a mixture of chlorine and steam under like circumstances yields HCl and oxygen gas (which seems to have been his principal object); the nitrogen gas obtained in either case is to be "passed over red-hot iron in a spongy state, by which the azote is absorbed; when hydrogen is brought on the combination of azote and iron thus formed, the decomposition is immediate, and a large quantity of ammonia is produced" (*sic*).

Henderson (patent No. 3080, 1871) passes a mixture of HCl and air over bricks or blocks of ferric chloride, made plastic by a little clay, heated to  $200^\circ$ . Or the HCl can first be passed over the oxide till it is saturated, and then heated air admitted, which again oxidizes the iron and liberates chlorine. The latter is brought into contact with fine lime-dust in revolving cylinders.

This process is founded upon the same reactions as those of Longmaid, Macfarlane, and Königs (comp. below, *sub* No. II.), but adds the *constant* action of ferric oxide, which is only the carrier of the reaction; and, on the other hand, it has analogy with the processes employing cuprous chloride and those with porous indifferent bodies in a red-hot state, among which it is enumerated in this place.

Weldon (patent No. 2170, 1871) passes a mixture of HCl vapour and atmospheric air over platinized asbestos or another platinized porous substance.

Wigg (No. 1725, 1873) proposes pumice, Townsend (No. 3483, 1874) manganese or magnesia compounds, for the same object. Aubertin (No. 1181, 1871) passes HCl and air over chromic oxide.

A general investigation of the mutual action of hydrochloric acid and oxygen in the presence of certain metallic compounds has been made by Lamy (Bull. Soc. Chim. 1873, vol. xx. p. 2). His results are as follows:—1st. All compounds of copper, iron, manganese, and chromium, and all compounds containing only traces of these elements, as pumice, porcelain, silica, glass, always yield a current of chlorine if they are heated and a mixture of hydrochloric acid and oxygen or air is passed over them. 2nd. The yield of chlorine in proportion to the HCl employed is dependent upon the nature of the active substance, the temperature, the composition of the gaseous mixture, and the rapidity of the gaseous current. 3rd. If oxides or chlorides are not employed directly, the salts are decomposed, *e. g.* cupric sulphate yields first oxide, then chloride. 4th. The quantity of the oxide liberated or the chloride formed is very slight in proportion to the quantity of chlorine gas produced. 5th. Under like conditions the yield of chlorine decreases as the rapidity of the gaseous current increases. 6th. On employing copper-salts the decomposition is at its maximum at about 440° C. At this temperature and with mixtures of HCl and O or air which contain from 60 down to 4 per cent. of HCl, the yield of chlorine varies from 20 to 95 [?] per cent. At the temperature of boiling mercury no chlorine is evolved. 7th. Under like conditions the oxides of manganese, iron, or chromium yield only half as much chlorine as copper; but at a low red-heat or near the melting-point of glass the yield of chlorine is 50 to 75 per cent.  $Mn_2O_3$  yields more chlorine than  $Fe_2O_3$ ; the chlorides

of the former are also less volatile. 8th. Common pumice at 350° C. yields no chlorine, at 440° C. 15 per cent., at a red heat 30 per cent. When purified from iron by hydrochloric acid, it yields extremely little chlorine. 9th. Porcelain, apparently pure silica, Bohemian glass, and alkaline chlorides (impure) yield only a small percentage of chlorine at the heat of fusion of glass, ferric chloride being volatilized.

The processes in which the oxidation of the hydrogen in HCl is effected by atmospheric oxygen, always in the presence of "catalytic substances," cannot be sharply distinguished from those in which the oxidation first goes on with the manganese &c., as both reactions are sometimes carried on in succession. We shall therefore consider these combined processes in this place.

#### *Weldon's Magnesium-Manganite Process.*

This process (Engl. pat. 2389, 1871; 317 & 2044, 1872) was worked out by Weldon, in order to avoid the objection justly made to his classical manganese recovery process, that in the latter two-thirds of the hydrochloric acid are lost in the shape of calcium chloride and only one-third is obtained as free chlorine. The process in question roused many expectations; but as these have not at all been fulfilled, I must refer to the detailed description and illustrations given in the first edition of this work, vol. iii. pp. 237 to 247; only a brief outline will be given here. Acid manganese liquors are saturated with magnesite, the settled solution is boiled down to that point at which HCl would begin to be given off, *i. e.* about 160°. The further treatment takes place in a reverberatory furnace, in which the mixture of manganous and magnesium chloride is brought to dryness, with evolution of much HCl and a little free chlorine, which is condensed by water to liquid hydrochloric acid. The dry residue, consisting of  $\text{MnCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{MgO}$ , and  $\text{MnO}$ , is heated in a second furnace in a current of air at "blood-red heat;" here free chlorine is given off, with a little HCl, and magnesium manganite,  $\text{MgMnO}_3$ , remains behind in the shape of a dense black powder, always containing an excess of base. This is treated with hydrochloric acid in stone stills exactly like ordinary Weldon mud; chlorine is liberated, and a mixed solution of  $\text{MgCl}_2$  and  $\text{MnCl}_2$  is formed, which is neutralized with magnesia and again introduced into the cycle of

operations. Thus part of the chlorine is obtained in the concentrated, part in the dilute state, and there is little or no waste.

In this shape the process seemed to be very imperfect, and Weldon (Engl. pat. 222, 964, 965, 966, of 1881) tried to improve it by mixing the partially boiled-down solution of manganese and magnesium chloride with solid magnesium manganite from a former operation, in order to obtain a more porous mass on drying. A revolving furnace for this process is described in the patents Nos. 4079 and 5868, 1883. As Weldon has informed me himself, the only reason for not following up this process was that the employment of manganese had been found to be quite unnecessary; comp. the Péchiney-Weldon process, *sub* No. IV. of this Chapter.

Townsend (Engl. pat. 3483, 1874) described a very similar process.

Bückse (Engl. pat. No. 16320, 1894) performs the magnesium-manganate process in vertical retorts, heated to a red heat, into which is introduced at the top the mixture of 1 mol.  $\text{MnCl}_2$  and 0.8 mol.  $\text{MgCl}_2$ , containing 25 or 30 per cent. water, together with air and superheated steam; at the bottom  $\text{HCl}$  escapes and the compound of  $\text{MgO}$  with  $\text{MnO}_2$  is withdrawn in the shape of porous lumps, easily soluble in hydrochloric acid without external heating and leaving no residue.

#### *De Wilde and Reyckler's Process.*

This process (Engl. pat. 17272 and 17659, 1889) employs both magnesium and manganese compounds, but it has also considerable analogy with the Deacon process, and it can in fact be carried out almost entirely in an ordinary Deacon plant. It is based on the following facts (taken from a pamphlet published at Brussels in July 1890, and republished in the 'Moniteur Scientifique,' 1890, p. 1109).

If equivalents of the following substances are fused together :

Epsom salts .....	$\text{MgSO}_4, 7\text{H}_2\text{O}$
Crystallized magnesium chloride ...	$\text{MgCl}_2, 6\text{H}_2\text{O}$
„ manganous chloride ...	$\text{MnCl}_2, 4\text{H}_2\text{O}$

and by further heating the water of crystallization is expelled, much  $\text{HCl}$  goes along with this, and the residue forms a reddish-

grey, hard, friable, very hygroscopic mixture of  $\text{MgSO}_4$ ,  $\text{MnCl}_2$ , and  $\text{MgO}$ ,  $\text{MgCl}_2$ , almost anhydrous. If this mixture is heated in a muffle to a dark-red heat in the presence of air, both  $\text{HCl}$  and chlorine escape, and the residue is a black, porous, hard mixture of anhydrous magnesium sulphate and magnesium manganate,  $\text{Mn}_2\text{O}_3\text{Mg}$ . If this is heated to about  $425^\circ \text{C}$ . and a current of  $\text{HCl}$  is passed through, at first a very regular current of chlorine and water escapes, which is gradually mixed with more and more unchanged hydrogen chloride. The reaction is:



The magnesium sulphate does not enter into the reaction. Here, therefore, *one-fourth* of the chlorine is given off, and that in the concentrated state. The residue is heated rather higher, to about  $525^\circ \text{C}$ ., and a current of dry air is passed through. Now, again, chlorine is given off, but diluted with air:



Thus the magnesium manganite has been re-formed in its mixture with the unchanged magnesium sulphate; it is once more treated at a rather lower temperature with  $\text{HCl}$ , then again with air, and so forth.

If during the treatment with  $\text{HCl}$  the temperature rises too much, oxygen is liberated, all the more the higher the temperature, the reaction being:



The inventors state that they obtained, with an experimental apparatus containing 18 cwt. of converting-substance, and 7 ft. 8 in. high, a decomposition of 76 per cent. of the  $\text{HCl}$ . During the period of oxidation the gas contains on an average 18 or 20 per cent. chlorine by volume, and 1 or 2 per cent.  $\text{HCl}$ , the latter owing to the moisture of the air; later on the gas is weaker. With 18 cwt. of converting-substance, 3 cwt. of chlorine can be made in 24 hours. In order to make a ton of chlorine per day, 6 tons of substance would be required, against 30 tons of contact substance contained in a Deacon apparatus. Only 6 per cent. of the  $\text{HCl}$  is absolutely lost; that which is not converted into chlorine is recovered as acid of  $30^\circ \text{Tw}$ .

This process would from the first attain a decomposition of upwards of 70 per cent. of the HCl, and would turn out part of the chlorine altogether pure, and the remainder more concentrated than Deacon chlorine.

The inventors believe that by their process they can produce twice as much chlorine with the same cost of plant as the Deacon apparatus (£6000 for 18 or 20 tons bleaching-powder per week). The contact mass is nothing like so sensitive as Deacon's, and its eventual renewal costs very little. They give the following estimate of the cost of 1000 kil. of chlorine (without details) :—

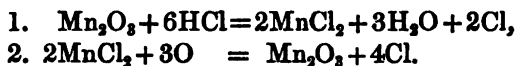
1333 kil. gaseous HCl .....	109 francs.
Coals, wages, repairs .....	47 „
	<hr/>
	156 „

This suffices for nearly 3 tons of bleaching-powder [here it is overlooked that about 10 per cent. of the chlorine is lost in the manufacture of bleaching-powder].

A new patent of De Wilde, Reyckler, and Hurter (No. 20284, 1892) describes a decomposer, divided into several compartments, one above the other, and separated by earthenware or iron grids; the gas enters at the top and leaves at the bottom. The decomposed mass can be renewed without any interruption of work by means of man-hole doors, lined with earthenware, in connexion with each compartment. If air and HCl are introduced at the same time, a single decomposer suffices; but if hot air and HCl gas are introduced one after the other, it is preferable to employ several decomposers to serve in turns.

*Chlorine from Hydrochloric Acid after conversion into Magnesium or Calcium Chloride, &c.*—All processes for manufacturing chlorine from magnesium chloride, &c., can be equally applied to hydrochloric acid, *e.g.* by allowing it to act upon MgO, which is always recovered later on. But it is not possible to carry this out economically, as has been especially proved in working out the Péchiney-Weldon process. If once free hydrochloric acid has been obtained, it is best to submit this to one of the previously known processes. The new processes could only be thought of for otherwise valueless chlorides, like the CaCl, from the ammonia-soda manufacture, or the MgCl, in Stassfurt mother liquors; these will be described further on (III. and IV.).

*Chlorine from Manganous Chloride and Oxygen.*—When Weldon was working out his magnesia-chlorine process (p. 558), he noticed that dry manganous chloride by itself can be completely decomposed by oxygen and converted into  $Mn_2O_3$ . This had been long before patented by Barrow (No. 485, 1855); also by Tessié du Motay (Nos. 470 and 2232, 1871). Weldon's own patents are Nos. 4079 and 5868, 1883. If a solution of neutral  $MnCl_2$  is carefully brought to dryness at temperatures not exceeding  $200^\circ C.$ , it is not decomposed, contrary to the ordinary assumption, but it yields pure, dry  $MnCl_2$ . If this is heated in a current of air to a dark-red heat, we obtain  $Mn_2O_3$  and free chlorine. But in order to make this decomposition complete, we must prevent the mass from fusing by mixing it with its own weight of the residue from a previous operation. The  $Mn_2O_3$ , when treated with hydrochloric acid, yields more chlorine,  $MnCl_2$  being re-formed. The reactions are:—



Hence all the chlorine is liberated: one-third (by equation No. 1) in the concentrated state; two-thirds (No. 2) diluted with nitrogen and excess of air, but rather less than Deacon gas, viz. containing 7 or 8 vol. per cent. pure chlorine.

This process is very fine in theory, but failed in practice. The pulverulent  $M_2O_3$  cannot be treated like manganese ore or Weldon mud, and is very imperfectly decomposed by hydrochloric acid. In order to make use of the very acid still-liquor obtained, it had to be neutralized with hydrated manganous oxide, precipitated from  $MnCl_2$  by lime, which means losing the corresponding Cl as  $CaCl_2$ . A second drawback is that the mixture of  $MnCl_2$  and  $Mn_2O_3$  is too friable. Whatever means may be employed for moulding it into lumps, these soon fall to pieces during the reaction of the hot air (the temperature is about  $700^\circ$ ), and the air does not then penetrate through the mass. It was tried to employ a retort turning round a horizontal axis, but this also failed, and the process had to be given up, although it had been found that manganous chloride is one of the chlorides most easily decomposed by air (Gall, in Wurtz's Dict. de Chim., 2nd Supplement, i. p. 1089).

The Péchiney-Weldon magnesium-chloride process was also



originally intended for application to Leblanc hydrochloric acid. But as the inventors soon convinced themselves that this would hardly pay, and that it must find its essential application upon magnesium chloride, either from Stassfurt, or from the mother liquors of the sea-water salt-gardens, or from the manufacture of chlorate of potash, we shall refer to it under magnesium chloride (No. IV.).

*Chlorine from Manganous Chloride and Ferric Oxide, &c.*—Macfarlane (Engl. pat. 9234, 1884) evaporates a solution of  $\text{MnCl}_2$  to dryness, grinds the residue to powder, mixes with 1 to 4 parts of ferric oxide, and heats in a muffle, with stirring, in a current of dry air to  $400^\circ\text{C}$ . Chlorine and a little  $\text{HCl}$  is evolved; the residue contains the ferric oxide with  $\text{MnO}_2$  or  $\text{Mn}_2\text{O}_3$ . When treating it with hydrochloric acid, chlorine is liberated and  $\text{MnCl}_2$  is re-formed; the  $\text{Fe}_2\text{O}_3$  is not acted upon.

Very similar to this is Bramley's patent (No. 8289, 1887); he proposes to utilize the residual mixture of ferric and manganic oxide in the manufacture of iron or steel.

Similar patents are those of the Verein für chemische Industrie in Mainz (Engl. pat. 3322, 1886, comp. *sub* No. V., ammonium chloride) and of Burns (No. 15488, 1886).

*Chlorine by Ferrous or Ferric Chloride and Air.*—Thibierge (Engl. pat. 2290, 1855) passes dry  $\text{HCl}$  gas over heated iron, and conveys the hydrogen formed into a gas-holder. The  $\text{FeCl}_2$  is exposed in the same vessel to the action of a current of dry air, and by this decomposed into ferric oxide and chlorine.

The same action is also utilized in the patent of Macfarlane of 1863 (compare this); on it also are based those of Longmaid, Königs, Henderson, and others.

Swindells and Nicholson (Engl. pat. 390, 1852) pass oxygen, obtained by the baryta process, with or without atmospheric air through heated  $\text{MnCl}_2$  or  $\text{FeCl}_3$ , in order to prepare chlorine.

Larkin and White (pat. 3093, 1870) patent the manufacture of chlorine in general by passing dry air over anhydrous, red-hot magnesium or ferric chloride or other suitable chlorides. A continuous process is to be carried on as follows:—A current of  $\text{HCl}$  is passed over a hot metallic chloride (or metal); when this has been superficially converted into chloride, atmospheric air is passed through the same chamber, the  $\text{HCl}$  in the meantime passing into a second chamber, &c. Larkin, Leighton,

and White (pat. 1518, 1871) describe the manner of obtaining the ferric chloride for the above purpose.

*Mond's Nickel-Oxide Process.*

Mond's Engl. pat. No. 8308, 1886, describes the process as follows:—Gaseous HCl is brought into contact at a high temperature with nickel oxide (the other metallic oxides mentioned in the specification have apparently never come into use), which produces the chloride, the water escaping. If the product of the reaction is treated with heated air, the original oxide is regenerated and chlorine is set free. The nickel oxide is moulded into lumps; or pumice is impregnated with nickel chloride in the fused state or in solution, and by heating in a current of air NiO is made from it. This contact substance is placed in earthenware or in cast-iron retorts lined with fire-proof material, in which it remains once for all. Here alternately a current of heated hydrogen chloride gas and one of heated dry air is injected, then again HCl and so forth. It is stated that the HCl is completely converted into chlorine, and that more dilute and impure gas than with the Deacon process can be employed.

If this assertion had been correct, Mond's process would have at once replaced Deacon's, on the supposition that the loss of nickel by volatilization and by the contact substance becoming inactive did not prevent it; as nickel is much dearer than copper, this was certainly a very important point. At all events the nickel process never emerged beyond the experimental stage. It was possibly from the first not intended to be applied in the Leblanc process, but only as an adjunct to the similar process intended for making chlorine from ammonium chloride, which we shall describe *sub* No. V. It has never entered into serious competition with the Deacon process.

A similar claim for producing chlorine gas, almost free from HCl, from a mixture of HCl and air, is raised by Eschellman and Mond's patent (No. 17273, 1887), in which the contact substance is a mixture of magnesia, with 5 or 10 per cent. sodium or potassium chloride, and 5 or 10 per cent. of china-clay; the temperature of treatment to be between 450° and 550°. We describe this process also *sub* No. V. (Ammonium Chloride). So much is certain, that the just-mentioned contact substance has not yet replaced Deacon's.

*Manufacture of Chlorine by means of Nitric Acid or Nitrates.*

Watt and Tebutt (Engl. pat. 7531 & 7538, 1838) produce chlorine by heating lead chloride with nitric acid, or from common salt and nitric acid, with or without adding protoxide of manganese or lead or chromic acid, or by heating common salt with nitrate of baryta or lead, &c.

We again meet the heating of common salt with nitric acid in the patent of MacDougal and Rawson (No. 12333, 1848), which otherwise treats of the manufacture of chlorine by the aid of chromates (p. 554). Here we also meet with the recovery of nitric acid from the lower oxides of nitrogen, whichever way these may have been obtained, by the aid of air and water.

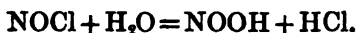
Binks (No. 7963, 1839) makes chlorine by passing 4 vols. of hydrogen chloride gas and 1 vol. of the gases obtained by heating nitrate of soda at a red heat through red-hot stoneware pipes; thus a mixture of chlorine, nitrogen, and water is obtained with undecomposed HCl, which is removed by washing. In the same manner chlorine, carbon monoxide, and water is obtained from 1 vol. HCl gas and 2 vols. carbonic-acid gas.

The first patent in this direction which was turned to real use was that of Dunlop (No. 11624, 1849), already mentioned (Vol. I. p. 414), in which a mixture of common salt and nitrate of soda is heated with sulphuric acid in iron cylinders, and the mixture of gases evolved is passed first through sulphuric acid, where the nitrous vapours are retained, then through water, where the HCl is washed out, and ultimately free chlorine is left. (Exactly the same process was patented by Roberts and Dale nine years afterwards, No. 2242, 1858.) This process has been actually worked for many years at Tennant's works at St. Rollox.

Dunlop's process, as well as the more recent nitric-acid processes, has been submitted to a laboratory investigation by myself, in conjunction with Pelet (Zsch. f. angew. Chem. 1895, p. 3), to which paper we shall again refer in the following pages. Since all these processes are based on the reaction going on in *aqua regia*, a beginning was made with an investigation of the latter. We found that H. Goldschmidt's view, put forward in 1879, is correct, the reaction being :



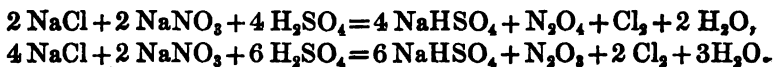
The nitrosyl chloride, in contact with water or sulphuric acid, is decomposed as follows :



These equations, however, express only the ultimate result, and that only approximately ; in the single stages of the evolution of gases the proportions more or less deviate from those given above.

In Dunlop's process the mixture of chlorine and nitrous gases is passed through moderately strong sulphuric acid ; the chlorine passes through unchanged, and is worked up into bleaching-powder, the nitrous gases are retained by the sulphuric acid ; the "nitrous vitriol" produced has the same value for the manufacture of sulphuric acid in lead-chambers as the corresponding quantity of nitric acid. The oxygen contained in the latter in excess over the nitrous gases has served for oxidizing the H of HCl and for liberating the *total* chlorine. This advantage is lessened by the drawback that much more sulphuric acid is consumed than in the ordinary saltcake process, that the process must be carried on in closed iron cylinders, and that the value of the "nitrecake" produced is everywhere much less than that of ordinary saltcake, sometimes *nil*. This, as well as the difficulty of disposing of such a large quantity of nitrous vitriol, explains why Dunlop's process has not extended to other works. At the then ruling prices of manganese ore and bleaching-powder, it seems to have been remunerative at St. Rollox, but even there it has long since been abandoned.

The reactions going on have been represented by one of the two following equations :—



In the first case twice as much nitre and  $\frac{1}{3}$  more sulphuric acid is used than in the second, for producing the same quantity of chlorine. Probably on the large scale the proportions employed have been nearer the second equation, except that less acid has been used, in order to produce nitrecake of the ordinary kind (not real bisulphate).

In our laboratory experiments the reaction passed essentially as follows :—



that is, exactly as with *aqua regia*. The temperature rose to 800°. The NaCl was almost entirely decomposed. Of the chlorine we obtained in the free state 66·72 per cent., as HCl 27·5–32·7 per cent. The nitric acid could be recovered with small loss—partly as such (15–24 per cent.), partly as nitrosyl-sulphuric acid (69·6–75·8 per cent.).

Tessié du Motay (Bull. Soc. Chim. xxii. p. 48) passes the gases evolved on heating NaCl, NaNO<sub>3</sub>, and SO<sub>4</sub>H<sub>2</sub> through cuprous chloride. CuCl<sub>2</sub> and NO are formed; the latter is to be mixed with hydrogen and converted into ammonia by red-hot platinized pumice; by heating the CuCl<sub>2</sub> to 200° or 300° it is to be decomposed into Cu<sub>2</sub>Cl<sub>2</sub> and Cl.

*Aqua regia* proper is the subject of the following patents:—

Swindells and Nicholson (No. 390, 1852) heat hydrochloric with nitric acid, and bring the vapours into contact with oxygen; in contact with water, nitric acid is formed, and chlorine is evolved.

Baggs and Simpson (No. 2313, 1864) heat hydrochloric and nitric acids together, pass the evolved chloro-nitric and chloro-nitrous gas through oil of vitriol, where the nitrous acid is retained and chlorine is liberated in order to be used in the ordinary way. The nitrous vitriol is decomposed by dilution with water and agitation, and the nitrous gas evolved is reconverted into nitric acid by the action of air; the vitriol is concentrated by evaporation and used over again.

Another patent of Baggs's, No. 3269, 1866, mentions in addition cooling appliances, &c.

The process of Wallis (Engl. pat. 13822, 1892) is as follows:—A mixture of (liquid) hydrochloric and nitric acid is made to enter a "decomposing cell," charged with sulphuric acid, from below, so as to bring about a good mixture, which can be also promoted by mechanical means. When the evolution of gas slackens, it is revived by hot sulphuric acid. Compressed air may also be passed through the apparatus. The gases are conducted through receivers charged with sulphuric acid, where NOCl and N<sub>2</sub>O<sub>5</sub> are retained, with formation of nitrososulphuric acid. From the NOCl is formed HCl, which can be recovered; but it is preferable to employ such an excess of nitric acid that all HCl is transformed into chlorine. The gas escaping from the receivers is treated for removing the HCl, first by weak hydrochloric acid, then by water; any traces

of nitrous acid are retained by NaCl, and ultimately there is only pure chlorine left. A further patent (No. 13047, 1893) adds the production of chlorine by the action of gaseous HCl on a concentrated solution of sodium nitrate or solid sodium nitrate, proceeding otherwise as above.

A new patent of the Wallis Chlorine Syndicate (Germ. pat. No. 84238) provides a cooling-tower between the decomposing-apparatus and the sulphuric-acid tower.

My laboratory investigation (comp. p. 565) proved the best temperature for Wallis's process to be  $120^{\circ}\text{C}$ .; we then obtained 76.44 per cent. of the chlorine in the free state. Any raising of the heat did not improve the yield. The remainder was found as HCl, evidently from the decomposition of NOCl. The nitric acid was found to be divided as follows:—from 61.64 to 78.76 per cent. absorbed in the sulphuric acid as  $\text{N}_2\text{O}_5$ , 4.25 to 4.83 per cent. as  $\text{HNO}_3$ , in the washing water 0 to 1.62 per cent., left in the retort 14.21 to 34.29, altogether found 99.42 to 100.28 per cent.

We tried to guard against this large residue of nitric acid left in the retort by adding at the close of the first operation some more sulphuric acid, together with more hydrochloric and nitric acid (in the proportions 2 : 1 or 2 : 2). The temperature was kept at  $90^{\circ}$  to  $96^{\circ}\text{C}$ . This did not give a greater yield of chlorine than before (66 to 69 per cent.), and quite as much nitric acid was left in the retort as formerly. This was, however, avoided by adding nothing but hydrochloric acid in the second stage; now only 0.46 per cent.  $\text{HNO}_3$  was left in the retort, and 1.96 per cent. was found in the sulphuric acid, besides 96.54 per cent. as  $\text{N}_2\text{O}_5$ . 64 per cent. of the HCl was converted into chlorine.

The above proves that nothing like all the HCl could be turned into free chlorine, even by an excess of nitric acid, and although the sulphuric acid aids the reaction by combining with the water. The reaction is the same as in Dunlop's process: first NOCl and  $\text{Cl}_2$  are formed; the former in contact with the sulphuric acid in the receivers yields  $\text{SO}_2\text{NH}$  and HCl. Later on free  $\text{HNO}_3$  distils over; this acts on the HCl in the receivers and yields a little more chlorine.

*If, however, from the first nitric acid is added to the sulphuric acid in the receivers, the state of matters is changed. In this case the HCl, formed by the decomposition of NOCl, meets with the*

necessary  $\text{HNO}_3$ , and is at once oxidized to chlorine. If about  $\frac{1}{3}$  as much nitric acid as was charged in the retort was added to the sulphuric acid in the receivers, it was possible to convert 90 to 95, or, allowing for the  $\text{HCl}$  remaining in the retort, up to 97 per cent. of the  $\text{HCl}$  into chlorine. It thus seems possible to attain to a practically complete decomposition of the hydrochloric acid on the large scale, if the nitric acid which condenses in the receivers is allowed to accumulate there, and the acid contained in the receivers is only removed at longer intervals. This could be done by employing a set of several receivers charged with sulphuric acid, the first of which may get saturated with  $\text{HNO}_3$ , while the following ones are still able to retain  $\text{N}_2\text{O}_5$ . In the first receivers the  $\text{NOCl}$  will be converted by the free  $\text{HNO}_3$  into free chlorine and  $\text{SO}_2\text{NH}$ .

In the process of G. & E. Davis (patents No. 6416, 6698, and 6831, 1890), the nitric acid is always recovered at once, and the condensation of  $\text{HCl}$  to liquid acid is avoided. They decompose common salt by sulphuric acid, preferably in a kind of mechanical furnace, separating the fuel gases from the  $\text{HCl}$ . The gases pass through several towers, packed with pumice &c. and fed with nitric acid, then through towers fed with sulphuric acid, then through a washing-tower fed with water, and at last through an aspirator, which draws the gases through the whole apparatus. The  $\text{HCl}$  gas, when meeting the nitric acid in the first tower, forms  $\text{Cl}$  and  $\text{NOCl}$ ; the latter is decomposed in a second or, if needful, in a third nitric-acid tower. The nitrous gases formed here are re-oxidized by air, introduced here, to nitric acid, so that the latter only acts as the carrier of atmospheric oxygen to the  $\text{H}$  of  $\text{HCl}$ . In their further progress the gases pass through sulphuric acid, where the nitrous gases are retained, and the chlorine passes on, which is washed with water in the last tower. The nitric acid is not to be stronger than  $80^\circ \text{Tw.}$ , in order to furnish the water necessary for the reaction. The sulphuric acid coming from the towers is employed for decomposing the common salt. The reactions taking place may be represented thus:—

- (1)  $3 \text{HCl} + \text{HNO}_3 = 2 \text{H}_2\text{O} + \text{NOCl} + \text{Cl}_2.$
- (2)  $\text{NOCl} + \text{HNO}_3 = \text{N}_2\text{O}_5 + \text{HCl}.$
- (3)  $\text{NOCl} + \text{H}_2\text{SO}_4 = \text{SO}_2\text{NH} + \text{HCl}.$
- (4)  $2 \text{HCl} + \text{N}_2\text{O}_5 = \text{N}_2\text{O}_3 + \text{H}_2\text{O} + \text{Cl}_2.$
- (5)  $\text{N}_2\text{O}_3 + \text{O} + \text{H}_2\text{O} = 2 \text{HNO}_3.$

Our laboratory investigation of Davis's process had the following results:—It is decidedly necessary to keep the acid in the nitric-acid receivers *hot* ( $80^{\circ}$  to  $95^{\circ}$  C.); the nitric acid must not be below  $80^{\circ}$  Tw., and a current of air must be passed through all the time. In this case the reaction is the same as with *aqua regia*, p. 565; 75 per cent. of the chlorine was obtained free, the remainder as HCl. The NOCl, formed especially in the first receiver, is driven forward by the heat and the current of gases; it does *not* act upon the nitric acid, or else it is always regenerated by the heat. In consequence of the higher temperature a little nitric acid is carried unchanged into the sulphuric acid, and reacts on the HCl there condensed or formed from the NOCl, so that instead of 66·7 per cent. of chlorine, to be expected according to the equation, up to 82·5 per cent. can be obtained, but only in presence of a current of air, which reoxidizes the nitrous acid formed from the NOCl.

Taylor's patent (No. 13025, 1884) describes a somewhat different process. The HCl gas from a saltcake-furnace is passed into a tower in which cold, strong nitric acid is running down. Here Cl, NOCl, and a little  $N_2O_3$  and  $N_2O_4$  are formed. The gases are passed into concentrated sulphuric acid, where the nitrogen oxides are absorbed, NOCl, with formation of  $SO_2NH$  and HCl. The mixture of HCl and Cl escaping is again passed through nitric acid, and once more through sulphuric acid, and this is repeated till nearly pure chlorine has been formed. The nitrous vitriol formed in the process is denitrated by water and a strong current of air; the gases are passed into water and the  $HNO_3$  is regenerated in this way. The  $HNO_3$  remaining in the sulphuric acid is obtained by distilling.

Taylor's process is very similar to that of Davis; but he tries to make the reaction more complete by repeated nitric-acid treatment of the gases issuing from the sulphuric acid, which on the other hand involves a more complicated apparatus and the employment of much more sulphuric acid. Davis, on his part, adds the action of air throughout the operation, and intends the recovery of nitric acid to be effected thereby *in loco*, while Taylor produces that recovery by a separate treatment of the nitrous vitriol.

In our laboratory experiments we found it best to employ three receivers, filled with nitric acid of spec. grav. 1·4, kept at  $80^{\circ}$  C., and to put between each of them and at the end sulphuric-acid receivers. Allowing for the chlorine left in the retort, we



obtained 96.53 per cent. free and only 3.47 per cent. as undecomposed HCl. Evidently at first  $\frac{2}{3}$  of the chlorine are set free:  $3\text{HCl} + \text{HNO}_3 = 4\text{H}_2\text{O} + \text{NOCl} + \text{Cl}_2$ . The NOCl yields the last 33.3 per cent. to the sulphuric acid as HCl; this, on the second passage, yields again  $\frac{2}{3} = 22.22$  free chlorine; the last 11.11 per cent. arrive as NOCl in the third apparatus, and  $\frac{2}{3}$  leave it as  $\text{Cl}_2 = 7.41$ ; total 96.30 per cent., which almost entirely agrees with the amount found.

We see that Taylor's process is a very good one, but only on the condition, *not* mentioned by the author, of *heating* the nitric acid. This process has been tried on the large scale, but not for a long time. Perhaps the failure was caused by not heating the nitric acid; perhaps there was too much moisture in the saltcake-gas, and the nitric acid became too dilute. That this is a drawback, we have proved in our experiments on Davis's process. Taylor's process consumes very much sulphuric acid, from which the nitric acid must be regenerated by a special operation. The apparatus is undoubtedly complicated, and very likely patience and money were exhausted before this promising process had been sufficiently worked out on the large scale.

Vogt and Scott (Engl. pat. 12074, 1893) describe the following process:—Dilute sulphuric acid, from a previous operation, is concentrated in an apparatus consisting of a set of dishes, and is run from the last dish into a tank. From this it runs into a horizontal or slightly inclined zigzag pipe. On the surface of the concentrated sulphuric acid there flows a stream of nitric acid in such manner that the two streams are not mixed. A current of HCl gas enters also from the top, all three acids travelling in the same direction. The apparatus is heated to  $125^\circ$ ; the gaseous products of the reaction are passed into a sulphuric-acid tower where the nitrogen oxides are retained; a second tower retains the HCl by means of water, so that pure chlorine remains. The mixture of sulphuric and nitric acids, issuing below, may be sufficiently strong for a second operation; if, however, the acid is too dilute, it is brought up to strength in a set of dishes.

My laboratory apparatus for testing this process consisted of a glass tube, 2 ft. 6 in. long, placed in a slightly inclined position in a calcium-chloride bath, both ends protruding from the bath. The upper end received, by means of an india-rubber stopper, the neck of a retort, in which HCl was evolved from NaCl and sulphuric acid; also two glass tap funnels for sulphuric and nitric acid. The lower

end was drawn out and communicated with a receiver for the running-down acids; the gases then passed through three bottles with sulphuric acid, two with water, and three with a solution of potassium iodide. The india-rubber stoppers were much acted upon by the hot gases.

In two experiments we obtained (a) 81.78 per cent. free Cl, 9.41 per cent. unchanged HCl; (b) 84.21 per cent. free Cl, 11.32 unchanged HCl; in both cases also 1 per cent. HCl left in the nitric acid. Allowing for the undecomposed NaCl, we had converted 85 per cent. of the Cl into the free state. About  $\frac{2}{3}$  of the  $\text{HNO}_3$  was found in the acid mixture running off at the bottom, viz. 0.80–1.88 per cent. as  $\text{SO}_2\text{NH}$ , 64.26–68.11 per cent. as  $\text{HNO}_3$ . The acid in the other receivers contained 13.76–20.29 per cent.  $\text{HNO}_3$  as  $\text{SO}_2\text{H}$  and 7.65–13.02 as  $\text{HNO}_3$ . Hence there was a great excess of nitric acid, and more of it was lost than in the previous trials, viz. 3.35–7.0 per cent. against 1 per cent. in the other processes (apart from Dunlop's). How much of this loss was caused by the action on the india-rubber it is impossible to tell.

Evidently in this as well as in Taylor's process first  $\frac{2}{3}$  of the chlorine had escaped as such,  $\frac{1}{3}$  as  $\text{NOCl}$ ; the latter had reacted in the receivers with the sulphuric acid and partly with the  $\text{HNO}_3$ , arriving there. The yield of free chlorine is good; the apparatus is simple, and the continuous style of work is a great advantage. But the considerable loss of nitric acid, probably caused by the high temperature (if not by the india-rubber), is objectionable; and the recovery of the large quantities of nitric acid getting mixed with dilute sulphuric acid is not very easy. On the large scale it may be easier than in my laboratory apparatus to keep the nitric acid in prolonged contact with hot sulphuric acid, and thus to utilize it better; or else to do this by more thorough contact with the current of gaseous HCl.

According to Donald's process (Engl. pat. 62, 1887) the HCl from a saltcake-furnace is dried by being forced through sulphuric acid; it then passes through a vessel, kept at a temperature of  $0^\circ$ , containing a mixture of strong sulphuric and nitric acid, where the reaction  $2\text{HCl} + 2\text{HNO}_3 = 2\text{H}_2\text{O} + \text{N}_2\text{O}_4 + \text{Cl}_2$  is produced, the sulphuric acid retaining the water formed in the reaction. The escaping gases ought not to be over  $30^\circ\text{C}$ .; they are passed by means of another injector through dilute nitric acid which retains the nitrogen oxides and oxidizes them to nitric acid by aid of a current of air. The first nitric-acid receiver is heated, the second

is kept at  $0^{\circ}$ ; both are connected by a tall pipe, provided with a number of balls, fed with water. The oxides not converted into  $\text{HNO}_3$  are retained in the last receiver by strong sulphuric acid.

This process differs from that of Wallis, in which a mixture of liquid hydrochloric and nitric acid is introduced into sulphuric acid. In Donald's process gaseous  $\text{HCl}$  acts upon a mixture of sulphuric and nitric acid.

Davis and Taylor also used gaseous  $\text{HCl}$ , but they make it act first upon  $\text{HNO}_3$ , and only afterwards, and indirectly, upon the mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  forming in the receivers. From Vogt and Scott's process that of Donald differs first as regards the temperature ( $0^{\circ}$  against  $125^{\circ}$ ), secondly by the fact that Vogt and Scott try to avoid the mixture of the nitric and sulphuric acids flowing in the same direction. Working at  $0^{\circ}$  must, by the way, be a rather expensive process on the large scale.

In examining Donald's process, we first tried how much dry  $\text{HCl}$  could be decomposed by a mixture of strong sulphuric and nitric acid, and found that more than 90 per cent. could be turned into chlorine. We then arranged experiments as nearly as possible like the specification, but varying the temperature. At  $0^{\circ}$  we got 38.6 per cent. free  $\text{Cl}$ , 3.9 per cent. escaping as  $\text{HCl}$ , 54.5 per cent.  $\text{Cl}$  and  $\text{HCl}$  remaining dissolved in the nitric acid. The nitric acid originally employed in combination with sulphuric acid was entirely reduced to  $\text{SO}_2\text{NH}$ ; the receivers contained  $\text{HNO}_3$ , as here the chlorine acted as an oxidizer. Since we found that at  $0^{\circ}$  the process did not work well, too much  $\text{Cl}$  and  $\text{HCl}$  being retained, we tried heating the nitric acid, and now we attained a decomposition of 94.9 per cent., only 2.53 per cent. of this chlorine being retained in the nitric acid. The nitric acid was disposed of as follows:—16.8 per cent. in the sulphuric acid as  $\text{SO}_2\text{NH}$ , 18.15 per cent. in the same as  $\text{HNO}_3$ ; 48.4 per cent. in the nitric-acid receivers; 12.8 as  $\text{SO}_2\text{NH}$  and 2.2 as  $\text{HNO}_3$  in the last sulphuric-acid receiver; loss 1.65. These results at the *higher* temperature must be regarded as good; but the recovery of the  $\text{HNO}_3$  as *strong* acid will be difficult, and there is again a very large quantity of sulphuric acid to bring up to strength.

A further patent of Donald's (No. 5488, 1890) prescribes dividing the stream of  $\text{HCl}$  gas in two equal parts, drying the gas and passing one half through a mixture of strong nitric and sulphuric acid, kept at  $0^{\circ}$ . Here a mixture of chlorine and  $\text{N}_2\text{O}_4$  escapes, which is again cooled down, mixed with the other half of

the HCl gas, passed through dilute nitric acid, where all  $N_2O_4$  and  $HNO_3$  is absorbed and nearly pure Cl escapes, which is further passed through nitric acid and at last through sulphuric acid. A current of air is introduced in a suitable place to oxidize the nitrous acid.

The Alkali Inspectors' Report, No. 26, p. 43, mentions that Donald's process had been tried for 18 months at a Widnes factory and again abandoned, but that hopes were entertained to make it work with suitable modifications (probably those embodied in the second patent). Report No. 30 (for 1893), p. 12, states that all further experiments had been abandoned. In 1895 the works were dismantled and the plans advertised for sale.

The Verein chemischer Fabriken (Engl. pat. 10604, 1894) describes a very similar process, also bringing the HCl gas from a saltcake-furnace in contact with a mixture of nitric and sulphuric acid. It is asserted that, if this is done at the ordinary pressure, the reaction is almost exactly  $HNO_3 + 8 HCl = NOCl + 2 Cl + 2 H_2O$ ; but under pressure, it is alleged, also  $N_2O_3$ ,  $NO_2Cl$  [both of which do not exist in the gaseous state], and  $N_2O_4$  are formed. It is further [quite erroneously] stated that  $N_2O_4$  and  $NO_2Cl$  pass unchanged through concentrated sulphuric acid, partly also through water, and that thus losses are caused. Therefore it is prescribed to employ pressure, by running the mixed acids down stone towers packed with acid-proof lumps, where they meet the HCl. In a similar apparatus, made of lead, the issuing gases are treated with strong sulphuric acid, which decomposes the NOCl; a third apparatus, made of earthenware and fed with water, regenerates  $HNO_3$  from  $N_2O_3$ .

Brand (Engl. pat. 11040, 1893) expels dry HCl from aqueous hydrochloric acid by sulphuric acid, and forces it through a number of vessels charged with a mixture of sulphuric and nitric acids; the NOCl and Cl formed here are passed through sulphuric acid and thus converted into nitrous vitriol and chlorine. [Where is the novelty?]

Sadler and Wilson's Engl. pat. No. 15866, 1894, for manufacturing chlorine from a mixture of sulphuric, hydrochloric, and nitric acids, presents as novel only some details of apparatus not possessing much importance. (This patent is criticised as containing in reality no patentable matter in Chem. Trade Journal, xvii. p. 175.)

Krause (Engl. pat. No. 16227, 1894) employs a "Glover tower," impregnated with hot sulphuric acid, kept between  $125^{\circ}$  and  $130^{\circ}$  C. by means of dry steam injected into the tower. The HCl gas is introduced at the top, together with nitric acid. Chlorine, nitrosyl chloride, and water are formed, the latter being absorbed by the sulphuric acid, whose temperature on leaving the tower should not be below  $125^{\circ}$  nor above  $130^{\circ}$  C., and whose strength should not be lower than  $90^{\circ}$ , but better about  $100^{\circ}$  Tw., to avoid losses. It is re-concentrated before use.

#### *Recovery of Nitric Acid from Nitrous Vitriol.*

In all nitric-acid chlorine processes a large quantity of sulphuric acid is employed which retains very much of the nitric acid, converted into nitrosyl-sulphuric acid,  $\text{SO}_2\text{NH}$ , the solution of which in sulphuric acid is technically known as "nitrous vitriol." Evidently the latter must be used over again in some way. In Dunlop's process this was done by employing it for working vitriol chambers; but this confines the process to a comparatively small limit. Such chlorine processes can only then be practicable if they "denitrate" the nitrous vitriol and regenerate both sulphuric and nitric acid, without much loss of the latter. There is no fear of losing any sulphuric acid; but it is always diluted, and must be reconcentrated. In order to clear up this question, I have (together with Pelet) made a number of experiments, with the following results (*loc. cit.* p. 565).

In our experiments we always employed 20 c.c. of nitrous vitriol, containing the equivalent of 3.610 grams  $\text{HNO}_3$  in the shape of  $\text{SO}_2\text{NH}$ ; this was denitrated by gradually introducing 80 c. c. water, drop by drop, in a constant current of air. On the large scale much less water is used, so that the resulting sulphuric acid contains 66 per cent.  $\text{SO}_4\text{H}_2$  and upwards; but we paid no attention to this, but only to the nitrogen oxides.

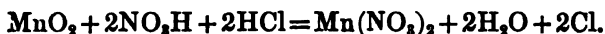
When trying to oxidize the escaping vapours by air alone, this was done very imperfectly, 52, or even 56, per cent. remaining in the state of lower oxides, according to the more or less perfect mixture with air. Our other experiments were made with air and water, as in actual practice. Behind the denitrating flask we placed two empty receivers, cooled by ice, then six receivers charged with water, and at last two or three charged with acidu-

lated potassium permanganate (to retain NO). A current of air was drawn in at three different places. The total loss of nitrogen never attained 2 per cent., part of which must be due to imperfect retention of NO by the permanganate. The latter retained 3 or 4 per cent. of the  $\text{HNO}_3$ , which must have reached it principally as NO. Adding this to the total loss, and taking account of the acid not expelled from the nitrous vitriol, we obtained in the water receivers in one, evidently imperfect, trial (where the denitration had also been imperfect) 90.29 per cent. as  $\text{HNO}_3$ , 1.35 as  $\text{HNO}_2$ , together 91.64 per cent. In two other, better conducted trials we recovered  $91.77 + 4.20 = 95.97$ , and  $93.15 + 0.95 = 94.10$  per cent. We therefore recovered on an average  $92\frac{1}{2}$  per cent. of the  $\text{SO}_3\text{NH}$  as  $\text{HNO}_3$  and  $2\frac{1}{2}$  per cent. as  $\text{HNO}_2$ ; nine-tenths of this was contained in the first empty receivers and the first two water-receivers. These results are decidedly good, and they may be expected to be fully realized, or even improved, on the large scale, when employing "plate-towers." Such a loss would not stand in the way of the nitric-acid chlorine processes, which certainly convert more of the HCl into chlorine than any other process hitherto practised on the large scale. Of course our laboratory experiments cannot be absolutely applied in actual manufacture, and they do not contribute to the important question of overcoming the enormous mechanical difficulties of the apparatus required for this class of processes.

*Chlorine by the assistance of Nitric Acid and Peroxide of Manganese.*

Schlösing (Compt. Rend. lv. p. 284) noticed that, by the action of a mixture of nitric and hydrochloric acids on manganese peroxide at a certain degree of concentration, chlorine is evolved, mixed with the reddish products from aqua regia; but at lower concentrations, even at a boiling heat, chlorine alone escapes and manganous nitrate remains behind. If the latter be calcined,  $\text{MnO}_2$  remains behind, and the escaping ruddy vapours can be reconverted into nitric acid by the action of water and air: thus both materials can be recovered and can be used again. The best proportions are:—4 equivalents of nitric acid containing 505 grams  $\text{N}_2\text{O}_5$  per litre, and 3 equivalents of hydrochloric acid containing 397 grams per litre: to the mixture one-seventh of its bulk of water is added, and the whole heated in a calcium-chloride

bath up to 122° C. Schlösing in this way obtained in two experiments 96 and 90 per cent. of the calculated quantity of chlorine; but the heating at first should not be too strong. The decomposition of manganous nitrate commences at 150°, and proceeds regularly at 175° or 180°; at 195° C. it is most vigorous. The remaining oxide is rather hard and close, and contains up to 93·3 per cent.  $\text{MnO}_2$ , along with a little lime and iron. Neither N nor NO is formed; and thus the complete recovery of the nitric acid depends only upon the completeness of the decomposition. On a small scale Schlösing obtained nitric acid of 62° Tw. and only lost 9 per cent. This process at that time did not get beyond the laboratory stage; but it deserved more attention, at any rate before Weldon's process had been worked out, especially as in it, as well as in Dunlop's very similar process, *all* the chlorine of the hydrochloric acid is obtained as such:



Schlösing's process had been partially forestalled by an English patent of Gatty's (No. 2230, 1857), who converts manganese sulphate or chloride into nitrate by adding potassium or sodium nitrate; the mixture is dried down, heated to a low red heat, and the vapours are passed into a lead chamber; the residue is washed with water, and black  $\text{MnO}_2$  is thus obtained.

Dow and Telfer (Engl. pat. 3089 and 3153, 1875) describe a process somewhat similar to Schlösing's. Instead of HCl, sodium chloride can be employed, and after heating the residue the sodium nitrate can be separated from the  $\text{MnO}_2$  by washing.

Without taking any notice of their predecessors, Just (Nos. 14857 and 14859, 1888) and Alsberge (French patent, noticed in my paper, Zsch. f. angew. Ch. 1889, p. 699) again patented the same process. An unimportant deviation in Alsberge's patent was the direction, first, to add to  $\text{MnO}_2$  half as much hydrochloric acid as in the old process:

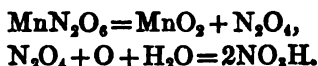


then to add nitric acid and not to heat beyond 105°:

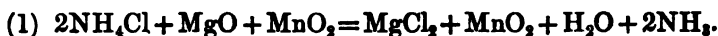


The further treatment is exactly as in Schlösing's process: heating

the residue to a dark-red heat and recovering the nitric acid, the reactions being :



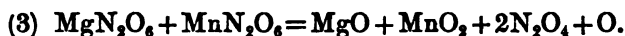
Alsberge (Engl. pat. 8779, 1889) also tried to combine this process with the ammonia-soda manufacture. The mother liquor from that process, first freed from ammonium carbonate in a column-still, and then containing principally ammonium chloride, is treated with the mixture of magnesia and manganese peroxide formed in a previous operation :



After driving off the ammonia, the residue is treated with nitric acid :



The residue is evaporated to dryness and ignited :



Of course the  $\text{N}_2\text{O}_4$  is regenerated to  $\text{HNO}_3$ . Lime may be employed instead of magnesia.

A further proposal of Alsberge's is this : the  $\text{NH}_4\text{Cl}$  liquor, freed from ammonium carbonate, is boiled down to dryness, and the residue is heated up to the sublimation of the  $\text{NH}_4\text{Cl}$ . The dissociated mixture of  $\text{NH}_3$  and  $\text{HCl}$  is conducted over finely divided  $\text{MnO}_2$ , heated a little below the temperature at which the ammonium chloride sublimes ; here the  $\text{HCl}$  is retained and the  $\text{NH}_3$  passes on :



The residue is treated with nitric acid as above ; that is, it is first heated moderately to expel the chlorine, then strongly to decompose the manganous nitrate, and so forth.

In this case, as the equation shows, free oxygen is evolved, which alone stamps the process as an irrational one. Alsberge's processes share the advantage of all nitric-acid processes in furnishing undiluted chlorine, but they would no doubt have encountered many difficulties had it been attempted to carry them out on a large scale (which was never done).

A supplement to Just's patent, otherwise exactly similar to



Schlösing's process, is contained in the U. S. patent No. 495462, of 1893. First hydrochloric acid is to be heated with twice its equivalent of manganese peroxide till it is completely decomposed, then sufficient nitric acid is added to decompose the  $\text{MnCl}_2$  formed, as well as the remaining  $\text{MnO}_2$ . The solution of manganous nitrate is neutralized with  $\text{MnO}$  or  $\text{MnCO}_3$ , settled, concentrated, dried in retorts and calcined; the escaping vapours are mixed with air and regenerated to  $\text{HNO}_3$ .

I have, together with Pret, studied the reactions of Schlösing's process (*Zsch. f. angew. Chem.* 1893, p. 99). I started from the following considerations. It cannot be assumed as impossible from the outset that the nitric acid lost would cost less than the lime and the compressed air in the Weldon process, assuming the wages to be the same and neglecting the cost of fuel for heating the manganous nitrate. But even in the more probable case that the value of the nitric acid lost and of the fuel exceeds the cost of recovering the  $\text{MnO}_2$  by the Weldon process, this expense might amount to much less than the enormous advantage of Schlösing's process, consisting in obtaining three times as much chlorine from the  $\text{HCl}$ , all of it in the concentrated state, and in having no waste to remove from the works.

The first objection which might be made to Schlösing's process is this: that the two reactions, the liberation of the chlorine and the decomposition of the manganous nitrate, might overlap. This objection Schlösing has answered by stating that these two reactions take place at entirely different temperatures, and can be kept under control as separate stages of the process. He states that he obtained from 90 to 96 per cent. of the chlorine of  $\text{HCl}$  in the free state, the recovered manganese peroxide tested 93.3 per cent.  $\text{MnO}_2$ , and 91 per cent. of the nitric acid was recovered. Evidently only a few experiments had been made, of which no analytical data are given.

Our laboratory experiments, described in detail *loc. cit.*, proved that the greatest possible quantity of chlorine can be liberated by employing an excess of 75 per cent. nitric acid over the theoretical quantity; it is best to add one-seventh volume of water to the mixture of acids and to employ a temperature of  $135^\circ$ . When adhering to these conditions, 98 or 99 per cent. of the theoretical quantity of chlorine could be obtained from the  $\text{HCl}$ . In this respect the process would be perfect, if the chlorine did not partially come

from  $\text{NOCl}$ . It would, however, be practicable only on condition of almost completely effecting the following reactions :—



It is indifferent, as regards the first of these reactions, whether we really obtain  $\text{N}_2\text{O}_4$  or  $\text{NO}_2$ , or the mixture of  $\text{NO}_2$  and  $\text{NO}$  representing  $\text{N}_2\text{O}_3$ , since all these are easily regenerated into  $\text{HNO}_3$  by water and air. An excess of  $\text{NO}$  is not so easily regenerated into  $\text{HNO}_3$ , as both our experiments and practical experience have shown.

We therefore tried first how far the  $\text{MnO}_2$  could be recovered in this case. We obtained in four experiments from 97·5 to 99·8 per cent. of the originally employed  $\text{MnO}_2$ , and we must therefore declare this part of Schlösing's process to be perfectly satisfactory. On the large scale the recovery would certainly not be carried on infinitely, as impurities would accumulate in the product.

So far as that most important point, the recovery of the nitric acid, is concerned, we succeeded in regaining from 84 to 90 per cent. of this acid. Part of the loss (7·5 to 8 per cent.) is already caused at the first stage, during the evolution of chlorine, part (2·5 to 8 per cent.) in the heating of the manganous nitrate. The former portion of loss will probably be quite as large in actual practice; the second will possibly be diminished by employing more perfect apparatus. The minimum loss of nitric acid in Schlösing's acid may be assumed to amount to 10 per cent.; probably it will be rather more, but hardly so great as the maximum which occurred in our experiments, viz. 16 per cent.

Wolters (Engl. pat. 16609, 1889) declares it to be possible to avoid loss of nitric acid in igniting the manganous nitrate, by distilling off the excess of nitric acid from the chlorine-still, employing the weaker fractions for condensing the  $\text{HCl}$  used in the process, and the stronger fractions, together with air, for recovering the nitric acid from the  $\text{N}_2\text{O}_4$  formed in heating the  $\text{MnN}_2\text{O}_6$ .

Wischin (Germ. pat. 54822) runs the liquor, obtained in evolving chlorine from  $\text{MnO}_2$ , hydrochloric and nitric acid, in a thin jet into cast-iron agitating-vessels, on the top of pulverulent  $\text{MnO}_2$ , at a temperature of  $200^\circ$ , so that no nitric-acid vapours can condense in the vessel itself, but the  $\text{HNO}_3$ , altogether vola-

tilizes and can be condensed outside. The liquor is absorbed up by the pulverulent  $\text{MnO}_2$ , and the fresh residue formed, also in the shape of powder, is mixed with that which had been originally employed, and forms no crusts. This avoids the difficulty of finding a suitable material for evaporating those liquors.

Bradburn (Engl. pat. 6710, 1889) mixes 2 mol.  $\text{NaCl}$  with  $4\text{HNO}_3$  and  $1\text{MnO}_2$ , and heats in an earthenware retort. The resulting mass is composed of  $\text{NaNO}_3$  and  $\text{Mn}_2\text{N}_2\text{O}_6$ ; the chlorine escapes in the free state. The residue is treated with caustic soda, which precipitates manganous hydrate; this is reconverted into  $\text{MnO}_2$  by air. The sodium nitrate is obtained in a solid form by evaporation, is mixed with ferric oxide and heated in a current of air. The nitrous fumes are passed over  $\text{MnO}_2$  and reconverted into nitric acid; by lixiviating the residue caustic soda is obtained; the ferric oxide is used over again. Instead of  $\text{MnO}_2$ , a manganate or permanganate may be employed.

## II. CHLORINE FROM COMMON SALT WITHOUT PREVIOUS PREPARATION OF HYDROCHLORIC ACID.

(The processes in which  $\text{NaCl}$  is employed mixed with  $\text{MgSO}_4$  are treated *sub* No. IV.)

*The Production of Chlorine by calcining Metallic Sulphides with Chlorides in the presence of an Excess of Air, i. e.* at the same time with  $\text{SO}_2$  and  $\text{SO}_3$ , is the subject of many patents which have for their object the simultaneous utilization of sulphur. They have accordingly been mentioned in treating of sulphuric acid and of saltcake. Longmaid's patent No. 10797, 1845, proposes at the same time to produce metallic oxides and chlorine by *calcining the chlorides* of manganese, copper, iron, zinc, or lead *with an excess of air*. Macfarlane (patent, No. 126, 1863) mixes 6 cwt. dried copperas with  $4\frac{1}{2}$  cwt. of decrépitated common salt and  $1\frac{1}{2}$  cwt. ferric oxide, heats the mixture in a muffle-furnace in a current of air dried by quicklime, and thus obtains sodium sulphate, ferrous and ferric chlorides; the latter are converted by the dry air into ferric oxide and chlorine. The chlorine is drawn by an exhauster through purifiers (boxes lined with lead and containing moistened pieces of coke) into wooden absorbing-boxes charged with slaked lime. The residual mixture of sodium

sulphate and ferric oxide is mixed with 214 lb. of coal and melted in a reverberatory furnace, the bottom of which has been lined with a mixture of ground quicklime and basic slag. The fused mass is lixiviated, the green solution decolorized by heating in the presence of gases rich in carbonic acid, and the solution of sodium carbonate worked up in the usual manner. The iron sulphide undissolved is to be converted into ferrous sulphate by the action of moisture and air [which is well known *not* to happen], and the ferrous sulphate obtained by dissolving and crystallizing. This part of the process is a modification of Malherbe's soda-process, afterwards revived by Kopp. The same process emerges once more in a patent of Königs (No. 1305, 1871): he moulds dried pyrites, common salt, ferric oxide, and water into bricks, which are dried and heated in a current of air—essentially Longmaid's process. A modification of this is patented by Königs and Henderson (No. 1642, 1871). Even in 1872 (No. 1540) Kenyon and Swindells patented the production of chlorine along with sulphuric acid from a mixture of rock-salt, sulphur, iron- or copper-pyrites, and a little nitrate of soda. Later on (No. 4013, 1873) they simply pass pure oxygen, together with "dry sulphuric acid," over heated common salt, in order to produce sodium sulphate and chlorine.

Hargreaves and Robinson (No. 668, 1870) pass heated air over a dry mixture of ferric chloride and common salt. According to No. 508, 1872, they mix common salt with chromium oxide for the same purpose.

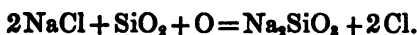
Weldon (No. 134, 1867) heats ferric sulphate with NaCl in a current of dry air.

Deacon (Engl. pat. 1908, 1871) mixes pyrites-burner gas with heated air, passes the mixture through clay marbles impregnated with a copper salt, and carries the  $\text{SO}_3$  thus produced, mixed with air, into chambers, where it forms with sodium or potassium chloride the respective sulphates and free chlorine. The escaping gas is re-conducted over the contact-mass until all the  $\text{SO}_3$  has been removed.

Daguin (Engl. pat. 3669, 1888) makes  $\text{SO}_2$  and air act upon chlorides in the presence of  $\text{MnO}_2$ , in order to produce chlorine.

Lalande and Prud'homme (Bull. Soc. Chim. 1872, p. 7; 1873, p. 74) generalized the reactions employed in Longmaid's process, by working not only with sulphuric anhydride, but also with *silica*,

*boric, stannic, phosphoric acid, and alumina.* If, for instance, dry air is passed over a red-hot mixture of silica with the chloride of an alkaline or earthy metal, chlorine is liberated and a silicate of that metal is formed :



If HCl gas is passed over the ignited mixture along with O or air, the silicate is always decomposed again, the chloride regenerated, and chlorine continuously given off. The aqueous vapour formed gives rise to secondary reactions : it is decomposed by chlorine into oxygen and hydrochloric acid ; it also decomposes the chlorides at a red heat into oxides and HCl. Between the quantities of chlorine, aqueous vapour, and hydrochloric acid which issue from the apparatus a state of equilibrium is probably produced ; so that the quantity of chlorine in proportion to that of HCl cannot surpass a certain maximum, which for lower degrees of temperature is probably a higher one. Pumice and broken bricks have a similar effect upon the liberation of chlorine as those acids, but not pipe-clay. The authors state that in their experiments they obtained as much chlorine as Deacon in his process with marbles saturated with cupric sulphate ; but in the latter case the reaction takes place at a lower temperature.

Gorgeu (Compt. Rend. cii. p. 1164), on heating 21 parts of NaCl with 79 parts of clay in a current of dry air, observed a partial decomposition of the NaCl ; the gas evolved was a mixture of 3 vols. Cl to 1 vol. HCl. 100 grams of NaCl yielded 25 or 30 grams Cl. He does not consider this reaction practicable on the large scale.

The process of S. G. Thomas, mentioned on p. 189, by which chlorides are treated with ferric oxide and pig-iron containing much silicon in a Bessemer converter, also belongs to this class.

Lieber (Germ. pat. 5610) moulds alkaline chlorides into lumps with kieserite and bauxite, and evolves HCl by means of steam, or Cl by means of air ; the residue consists of alkaline aluminates.

*Chlorine from Sodium Chloride and Air by means of Chromic Oxide* (Hargreaves and Robinson's patent, No. 508, 1872).—Sodium or potassium chloride is intimately mixed with chromic oxide, or with manganic oxide, and moulded into bricks. After drying, these are loosely stacked in chambers heated from without and brought to a red heat. By passing heated air over

them chlorine is liberated, or hydrochloric acid by air mixed with steam. The best mixture is 2 or 3 parts of  $\text{Cr}_2\text{O}_3$  to 1 part of  $\text{NaCl}$ . Instead of heating the chambers from without, the action may be produced by an additional heating of the entering air, the chambers being surrounded by bad conductors, *e. g.* magnesia bricks.

Arrott (Engl. pat. 2236, 1873) heats a mixture of common salt and *ferric phosphate* in a current of air, to obtain chlorine. The residue contains sodium phosphate and  $\text{Fe}_2\text{O}_3$ ; it is lixiviated; the liquor is treated with lime, to precipitate calcium phosphate and to obtain caustic soda; the calcium phosphate is heated with ferric chloride, obtained by dissolving the ferric oxide in hydrochloric acid.

Knight (No. 3261, 1871) heats *calcium phosphate* with  $\text{NaCl}$  in a current of air; chlorine is evolved and the residue contains sodium phosphate.

### III. CHLORINE FROM CALCIUM CHLORIDE.

In various processes of manufacturing chemistry calcium chloride is produced in enormous quantities as a by-product, formerly always regarded as an altogether valueless waste. This held good not merely of the dilute solutions, obtained in the manufacture of bicarbonate (Vol. II. p. 715), but also of the concentrated solutions obtained in the Weldon process and in the manufacture of chlorate of potash. But the circumstance that in the ammonia-soda manufacture vast quantities of calcium chloride are formed, which contain the total chlorine of the common salt, led to serious attempts to obtain this chlorine from the calcium chloride in the free state\*.

Most persistent efforts in this direction have been made by Solvay. His first patents (Nos. 77 & 171, 1877) prescribe mixing calcium (or magnesium) chloride with sand, clay, or a mixture of both, moulding in balls or the like, and treating with hot air in brick or iron towers, heated from without, in a methodical way, so that the air first comes into contact with the almost decomposed charge, and later on with the last fresh charge. The residue is to be utilized in various ways [none of them practicable!].

Later patents show developments of this process. Thus No. 838,

\* So far as the production of *hydrochloric acid* is concerned, the processes in question have been enumerated, Vol. II. p. 430 *et seq.*

1880, describes the furnace in which the decomposition takes place; Nos. 7258 & 7259, 1884, prescribe making the mixture of  $\text{CaCl}_2$  and silica less fusible by mixing it with the residue from a former operation, and replacing quartz sand by more active forms of silica. The apparatus is to be constructed of cast-iron, lined with a vitrifying coat. Patent No. 8724, 1885, prescribes adding to the mixture indifferent fire-proof substances, such as broken bricks, pebbles, &c., which absorb the heat of the gases, and in sinking down give it up again. The residue of lime, alumina, and silica is to serve for expelling the ammonia in the distillation of the ammonium-chloride liquors. Other descriptions of furnaces are shown in patent No. 13889, 1886. Patent No. 18574, 1888, states that alumina acts better than free silica, but it must be burned before mixing it with the calcium chloride, since otherwise the mixture could not be dried without evolving chlorine. In order to prevent the formation of carbonyl chloride, without heating too much, there is to be no heating from without, but the fuel gas, together with the necessary air, is to be blown into a high tower, provided with a jacket for preventing the loss of heat. In the centre of this tower the proper reaction



takes place; the upper part serves for retaining the excess heat of the fire-gases by fresh material, the lower part for giving up the heat of the residual material to the air, introduced for the sake of burning the fuel.

Solvay's German patent No. 50342 describes a cylindrical furnace turning on gudgeons. German patent No. 44865 extends the process to carnallite and kainite.

Twynam (Engl. pat. 731, 1885) treats  $\text{CaCl}_2$  liquors with 3 mols.  $\text{CaO}$  to 1  $\text{CaCl}_2$  at  $80^\circ \text{C}$ ., in order to form an oxychloride which is heated in a current of dry air, preferably in the presence of silica.

Bramley (Engl. pat. 8289, 1887) mixes  $\text{CaCl}_2$  with  $1\frac{1}{2}$  parts iron ore, and heats in a current of steam, to produce  $\text{HCl}$ , or of dry air, to produce chlorine. The residue, now containing the calcium as lime, is to be used instead of limestone in iron-smelting.

Lyte and Steinhart (Engl. pat. 21225, 1890) convert  $\text{CaCl}_2$  by  $\text{CO}_2$  and  $\text{MgO}$  into  $\text{MgCl}_2$ , and decompose this by the methods mentioned *sub* No. IV.

Basset and Elizade (French pat. 207465) convert  $\text{CaCl}_2$  into  $\text{MgCl}_2$  by boiling with  $\text{MgCO}_3$ ; comp. No. IV.

Taquet (Germ. pat. 30839) boils the calcium-chloride liquors down to dryness, and heats 500 kil. of the dry residue with 450 kil. ground  $\text{MnO}_2$ , and 550 kil. silica, to produce chlorine.

Compare also the other processes, mentioned Vol. II. p. 430 *et seq.*, in which  $\text{CaCl}_2$  is to be treated either for  $\text{HCl}$  or for  $\text{Cl}_2$ , by varying the conditions.

All processes for decomposing calcium chloride suffer from the drawback that the great heat of formation of  $\text{CaCl}_2$  from  $\text{Ca}$  and  $\text{Cl}_2$  renders its decomposition difficult, costly, and imperfect; in this respect it is greatly inferior to magnesium chloride, as we shall see *infra*. Hence proposals like that of Way (Engl. pat. 2139, 1869), to split up  $\text{CaCl}_2$  by steam alone into  $\text{CaO}$  and  $\text{HCl}$ , are utterly futile.

Hurter (Journ. Soc. Chem. Ind. 1883, p. 103) points out the great consumption of heat involved in the very best case by Solvay's calcium-chloride process. In this the  $\text{CaCl}_2$ , moulded with clay into lumps, is to be heated in a current of superheated steam, and the dilute  $\text{HCl}$  gas formed is to be freed from the excess of steam by calcium-chloride solution. Suppose we employ a solution containing 20 per cent.  $\text{CaCl}_2$ , and gas containing 5 per cent.  $\text{HCl}$ ; in this case a calculation shows that 10 tons of water must be evaporated for each ton of salt. To this we must add the superheating of the steam, and the heating of 1 ton  $\text{CaCO}_3$  and 1 ton of clay to red-heat. The reaction does not give out any heat; on the contrary, it consumes 26,000 heat-units per gram-molecule. After full consideration, Hurter believes that it would be cheaper to decompose the calcium chloride by sulphuric acid!

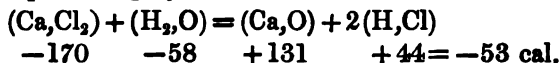
#### IV. CHLORINE FROM MAGNESIUM CHLORIDE.

We have seen Vol. II. p. 432 *et seq.* that magnesium chloride has been frequently proposed as a technical source for hydrochloric acid, and exactly the same holds good for chlorine. In both cases the fact is made use of that the decomposition of  $\text{MgCl}_2$  with water into  $\text{MgO}$  and  $2\text{HCl}$ , or with oxygen into  $\text{MgO}$  and  $\text{Cl}_2$ , is easier than that of calcium chloride. This is also explicable by thermochemical data.

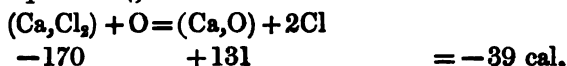


In the case of *calcium chloride* we find the heats of formation :—

(a) For producing hydrochloric acid :

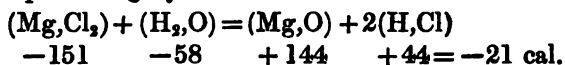


(b) For producing chlorine :

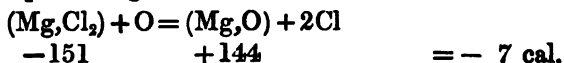


In the case of *magnesium chloride* :—

(a) For producing hydrochloric acid :



(b) For producing chlorine :



As it is not necessary for the purpose of comparing these two cases to take account of the consumption of heat for splitting off and evaporating the water of crystallization, we have not done so. A calculation including that item has been given for magnesium chloride in Vol. II. p. 434 ; it shows the theoretical consumption of heat for producing chlorine from  $\text{MgCl}_2$ ,  $6\text{H}_2\text{O}$  to amount to 107·6 calories.

Magnesium chloride is available for technical purposes from several sources, but by far the most abundant quantity is obtained as a waste product in the Stassfurt manufacture of potassium salts, which alone would be able to supply the world with all the chlorine at present required (Vol. II. p. 433). Large quantities of magnesium chloride might also be obtained from the mother liquors produced in the manufacture of salt from sea-water ; but this does not pay, in view of the conditions prevailing at Stassfurt. The latter would have led to the concentration in that locality of the greater part of the manufacture of chlorine produced at present in different parts of the world, if the efforts for cheaply extracting the chlorine from magnesium had been successful.

Very naturally other localities were not content that Stassfurt should have a monopoly of magnesium chloride. The process of Muspratt and Eschellmann (p. 537) for manufacturing chlorates by means of magnesia was rendered possible only by the fact that somewhat large quantities of magnesium chloride could be

disposed of; but this alone has prevented the process from extending beyond the place where it originated, in spite of its great advantages, because the application of magnesium chloride on a large scale has hitherto been only locally possible, viz. as a sizing for cotton-weavers (Townsend's patent), which application will hardly ever require more than 10,000 tons per annum.

Especially numerous have been the attempts at utilizing magnesium chloride as an intermediary product for making chlorine in the *ammonia-soda* manufacture. As it was well-known that chlorine (and hydrochloric acid) were at all events more easily and cheaply made from magnesium chloride than from calcium chloride, it was believed that the object of recovering the chlorine in that manufacture would be attained by decomposing the ammonium-chloride mother liquor by magnesia instead of by lime; the higher price of magnesia was no objection, as it was to be always recovered and used over again in the process.

Weldon was probably the first who proposed to utilize magnesia in the ammonia-soda manufacture. Before Solvay's processes had become at all known, Weldon (Engl. pat. 627, 1866, comp. p. 181) proposed to decompose sodium chloride by magnesium carbonate and carbonic acid into sodium bicarbonate and magnesium chloride, and to obtain from the latter  $\text{MgO}$  and  $\text{HCl}$  by heating, which is certainly not practicable. He was also one of the first (Engl. pat. 1539, 1872) to propose decomposing the ammonium-chloride liquors of the ordinary (Dyar and Hemming) ammonia-soda process by magnesia, instead of lime, in order to obtain  $\text{HCl}$  and  $\text{Cl}$  from the  $\text{MgCl}_2$ . Exactly at the same time Solvay (No. 1525, 1872) made the same proposal. In the same year (No. 2988, 1872) Young proposed decomposing the ammonium-chloride liquor by magnesium carbonate; and Weldon (No. 3805, 1873) repeats this, adding the recovery of the magnesia and of hydrochloric acid. The decomposition of  $\text{NH}_4\text{Cl}$  by  $\text{MgO}$  was once more patented by McDougall in 1886 (No. 2048). Cochrane and Bramwell (No. 11222, 1885) treat the  $\text{NH}_4\text{Cl}$  liquors first for magnesium oxychloride.

I have proved by laboratory experiments (Dingl. Journ. 1884, ccli. p. 36) that magnesia certainly is able to completely decompose solutions of ammonium chloride, but that this requires much more than the equivalent of  $\text{MgO}$ , and a much greater excess of  $\text{MgO}$  than of  $\text{CaO}$ . Practical men had recognized this long before, and

up to this day that reaction has not been attended with advantage in actual manufacture. Even if the Stassfurt competition did not make it hopeless to persevere in this direction, it could never be expected that the decomposition of ammonium chloride would be effected so easily, cheaply, and completely by magnesia as by lime, even on the supposition of recovering the magnesia from the magnesium chloride. This would have to be compensated by the recovery of the chlorine.

The following writers (all German) have published descriptions of the various processes for producing chlorine and hydrochloric acid from magnesium chloride:—Eschellmann (*Chem. Ind.* 1889, p. 2); Kosmann (Berlin, 1891); N. Caro (Berlin, 1893).

We shall now enumerate these processes, confining ourselves as much as possible to those treating of chlorine, since the production of hydrochloric acid from magnesium chloride has been already described in Vol. II.; but a strict separation is not possible.

The earliest mention which I can find of the decomposition of magnesium chloride by a current of steam with recovery of hydrochloric acid is in a patent of Tilghman's, No. 11556, Feb. 1, 1847, together with a mass of other things. He does not yet speak of chlorine. Immediately after, No. 11585, Feb. 19, 1847, de Sussex patents the preparation of chlorine by heating magnesium chloride with peroxide of manganese or with permanganates. The same is aimed at by a proposal made in 1855 by Ramon de Luna (*Compt. rend.* xli. p. 95), to produce chlorine by heating a mixture of magnesium sulphate, common salt, and peroxide of manganese;  $MnCl_2$  and  $MgO$  remain behind. We meet with the same in Binks and Macqueen's patent (No. 1240, 1860), but especially in Clemm's process (*Dingl. Journ.* clxxiii. p. 127). Crude  $MgCl_2$  liquor (from the Stassfurt mines) was to be evaporated to  $88^\circ Tw.$ , and mixed at a higher temperature with so much ground manganese that 1 mol.  $MnO_2$  would be present for every 2 mola.  $MgCl_2$ . The cooled and solidified mixture is crushed and exposed in large stone chambers to the action of steam superheated to  $300^\circ C.$  or upwards; chlorine gas is evolved, is purified from steam and  $HCl$  by an apparatus filled with manganese ore, and passes into a small gas-holder made of wood or gutta-percha, &c., which serves as collector or regulator before the gas passes into the absorbing-apparatus. This process has never become practical.

Townsend (*Engl. pat.* 1703, 1879) again mixes  $MgCl_2$  with

about 10 per cent. manganese oxides, and exposes the mixture to heated air at about  $113^{\circ}$ , preferably with addition of  $\text{CaCl}_2$ . According to a further patent (Germ. pat. 29307) he first produces  $\text{HCl}$  by heating a mixture of  $\text{NaCl}$ ,  $\text{MgSO}_4$  and  $\text{SiO}_2$  in a current of steam, mixes the  $\text{HCl}$  with heated air, and passes the solution over a porous mixture of manganese ore, magnesia, and clay, heated to  $205^{\circ}$ – $315^{\circ}$  in fireproof retorts.

Lyte and Steinhart (Engl. pat. 21225, 1890, comp. p. 585) produce chlorine by heating  $\text{MgCl}_2$  with Weldon mud; the presence of substances retaining the water is advantageous for the reaction. In the presence of sufficient moisture the evolution of chlorine is finished between  $150^{\circ}$  and  $350^{\circ}$ . The  $\text{HCl}$  evolved with the chlorine is separated from it by washing. A series of reactions is given, the final products being soft-burned magnesia, calcium carbonate, and chlorine.

Basset and Elizade (French pat. 207465, comp. p. 586) mix  $\text{MgCl}_2$  with its equivalent of  $\text{NaCl}$ , add  $\text{MnO}_2$ , and heat to a red heat.

The French patent of Wolters (No. 213974) is practically identical with Weldon's magnesium manganite process (p. 558).

We now come to the processes, working *without oxides of manganese*, which are more important. Solvay's patents, quoted *sub* No. III. (p. 584), were all taken out for  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , but he does not seem to have practically worked with the latter. The real development of the magnesium-chloride process is connected with the labours of Weldon, which were soon taken up by Péchiney, and led to the Péchiney-Weldon process, in the technical working out of which Boulouvard has taken a prominent share.

As early as 1868 (Engl. pat. No. 565) Weldon had proposed to apply  $\text{MgO}$  instead of lime in the recovery of  $\text{MnO}_2$  from  $\text{MnCl}_2$ , in order to obtain, instead of the  $\text{CaCl}_2$  going to waste in the ordinary Weldon process, a salt, viz.  $\text{MgCl}_2$ , from which  $\text{HCl}$  can be produced by heating. This part of his patent was disclaimed by Weldon on April 28, 1870, after he had convinced himself that Clemm (Engl. pat. 1776, 1863) had previously described a similar decomposition of  $\text{MgCl}_2$ ; but no doubt also because he had found that magnesia cannot easily replace the lime in the above process (comp. p. 588). At that time he intended to obtain  $\text{MgCl}_2$  from  $\text{CaCl}_2$  by treating it with  $\text{MgO}$  and  $\text{CO}_2$  under pressure, with formation of  $\text{CaCO}_3$  (Engl. pat. 732, 1869), but he did not pursue

this idea. Later on (No. 2389, 1871) he proposed to employ magnesia instead of lime in the manufacture of chlorate of potash, in order to produce HCl or chlorine from the  $MgCl_2$  formed.

About that time Weldon hit upon the idea of his magnesium-manganite process, described p. 558, in which, however, he started from Leblanc hydrochloric acid, magnesium chloride being only an intermediate product. While effecting improvements in this process (p. 559) the idea struck him to leave out the manganese altogether and to work exclusively with magnesium compounds (Engl. pat. 967 and 968, 1881). Here the chemical principles of the new process are already completely developed, especially the mixing of concentrated solutions of  $MgCl_2$  with solid magnesia (or ferric oxide, which has never been practically tried), and moulding the mixture into lumps which remain infusible and porous on heating, so that they permit the action of hot air upon their interior, and are also better conductors of heat. He at that time proposed a set of iron cylinders, lined with bricks, similar to a Hargreaves apparatus; but this was not found practicable, as the heat did not sufficiently penetrate into the mass.

The further working out of the technical details was taken over by Péchiney, with the assistance of Boulouvard, and was effected at Salindres. The different stages of his inventions are described in the English patents taken by him and Weldon in 1884 (Nos. 9305 & 11035) and in 1887 (Nos. 14653 & 14654).

A detailed description of the experimental plant erected at Salindres for the daily production of a ton of chlorine has been given by Dewar (Journ. Soc. Chem. Ind. 1887, p. 775), and this will be especially made use of in the following summary:—

**First Operation. Dissolving the Magnesia in Hydrochloric Acid.**—The  $MgO$  employed here is part of that recovered in the fifth operation. The HCl comes partly from the same source, partly from the Leblanc process. The temperature rises considerably, and the work must be performed slowly to avoid boiling. It is done in a "neutralizing well," as provided in the old Weldon process (p. 331). The acid runs in slowly and magnesia is added in small quantities; as soon as the heat rises too much the mass is allowed to cool down a little. Part of the magnesia may be replaced by the riddlings from sifting the magnesium oxychloride in the third operation, which otherwise cannot be directly utilized

and which lower the temperature. In the end a slight excess of magnesia is added, in order to precipitate ferric oxide, alumina, &c., and a little solution of  $\text{CaCl}_2$ , in order to convert into  $\text{MgCl}_2$  at least part of the magnesium sulphate formed by the sulphuric acid contained as impurity in the hydrochloric acid. The liquor is then allowed to settle.

**Second Operation. *Preparation of the Magnesium Oxychloride.***

—The solution obtained in No. 1 is boiled down to the point where only 6 mols.  $\text{H}_2\text{O}$  are present to 1 mol.  $\text{MgCl}_2$ , and is then converted into oxychloride in an apparatus of which fig. 176 shows a longitudinal section and fig. 177 a sectional plan. It consists of an annular iron vessel A, resting on rollers *a, a*. By means of the bevelled wheel *b* and pinion *c*, A is made to revolve slowly. M is an immovable frame on which three stirrers, G, D, E, and the shafts *d* and *f* are fixed. The stirrers are rotated from shaft *f* by means of a bevelled wheel gearing with another bevelled wheel on the central stirrer D, from which G and E are driven by other spur-wheels. The fast and loose pulleys B and B' transmit the motion from the steam-engine.

The boiled-down solution of  $\text{MgCl}_2$  is put into A, and is there mixed with  $1\frac{1}{2}$  equivalents of  $\text{MgO}$ . This  $\text{MgO}$  is brought by a chain of buckets which lets it descend through a strainer, under which the annular vessel containing the  $\text{MgCl}_2$  slowly rotates, the operation lasting about twenty minutes. The mass becomes very hard, with evolution of much heat, and is in the form of solid pieces of different sizes. It is discharged into little iron waggons, which by means of a lift carry it to an upper floor, where the reaction continues for some time. Its composition is approximately:—

Impurities ...	4.00
Water .....	41.16
$\text{MgCl}_2$ .....	35.00 = 26.16 per cent. Cl.
$\text{MgO}$ .....	19.84 = 1.346 equiv. per 1 equiv. of $\text{MgCl}_2$ .
<hr/>	
100.00	

**Third Operation. *Breaking, Crushing, and Sifting the Oxychloride of Magnesia.***—This substance must be reduced to pieces not larger than a walnut, but free from dust. It is

Fig. 176.

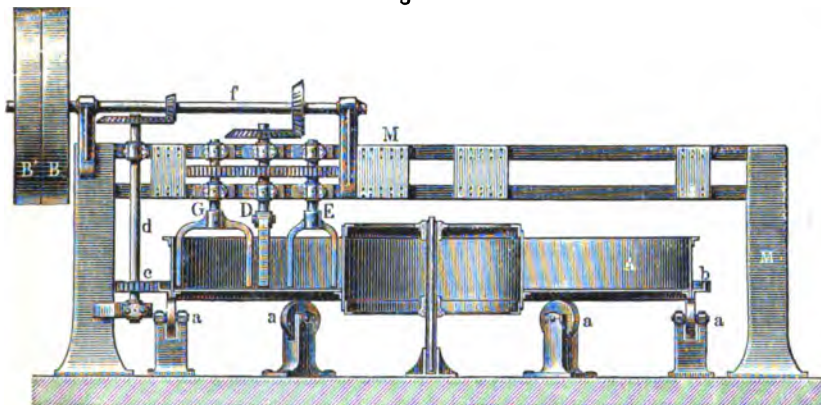
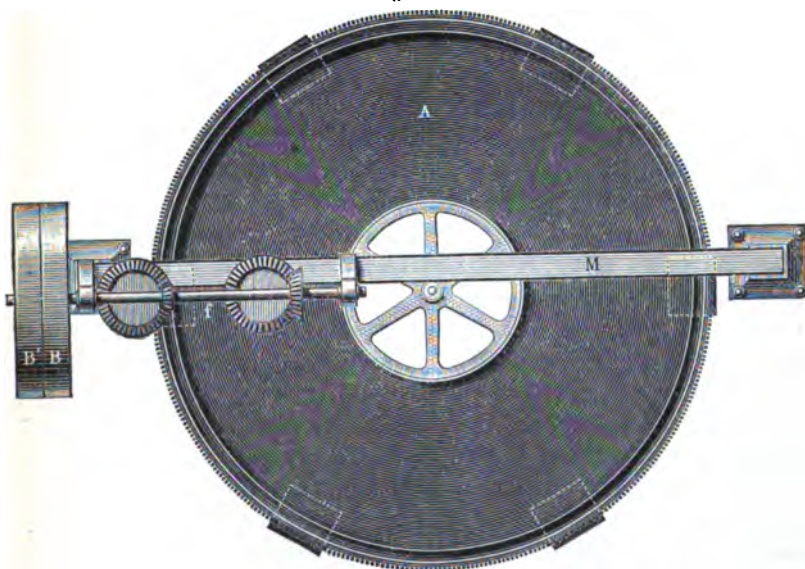


Fig. 177.



crushed by means of cylinders bristling with diamond points; it then falls into a rotary sieve, which separates from it all the particles less than 5 millimetres. About 20 per cent. is obtained in the shape of powder, part of which can be used in the first operation as described; the remainder returns into the second operation.

**Fourth Operation. *Drying the Oxychloride of Magnesium.***—This is necessary because otherwise less Cl and more HCl would be formed in the next operation, and the temperature could not be kept sufficiently high. A considerable quantity of water can be expelled without losing much HCl, but the temperature must not rise above 250° to 300° C, which can be secured only by means of a current of hot gases. The necessity of avoiding the formation of dust made it impossible to use mechanical agitators for the drying process. The apparatus employed for drying is shown, in cross and longitudinal section, in figs. 178 and 179. It consists of a brick flue through which the trucks filled with oxychloride pass, the oxychloride being spread in layers of 2 to 2½ inches thick on seven shelves in each truck, the hot gases traversing the flue in the opposite direction. The locks A and B prevent the trucks from entering or leaving without opening direct communication between the interior of the flue and the outer air. To introduce a truck, door *a* is opened, and is shut again after the truck has been put in the lock. Dampers *c* and *d* are then lifted, and by means of the pusher-rack G the truck is made to advance into the flue. It pushes truck No. 10 and the whole train of trucks forward, No. 1 being pushed partly into the exit-lock B; it is entirely drawn into this lock by the hook D worked from the outside. Damper *d* is then shut, door *b* opened, and the truck withdrawn by hand. The hot gases enter at M and leave the flue at N; their temperature must not exceed 300° C. A special, very ingeniously constructed, apparatus serves for spreading the oxychloride regularly on the seven shelves of each truck; for this we must refer to the original description.

During the drying, the oxychloride loses 60 to 65 per cent. of its water, together with 5 to 8 per cent. of its chlorine, in the shape of HCl; the dried product is therefore richer in magnesia than the original product. Thus, for instance, the oxychloride, the analysis of which has been given above, was found to be reduced by drying to 73·36 per cent., formed of:—

Impurities ...	5·47 per cent.
Water .....	21·62.
MgCl <sub>2</sub> .....	44·45 = 33·30 per cent. Cl.
MgO .....	28·36 = 1·511 equiv. of the MgCl <sub>2</sub> .



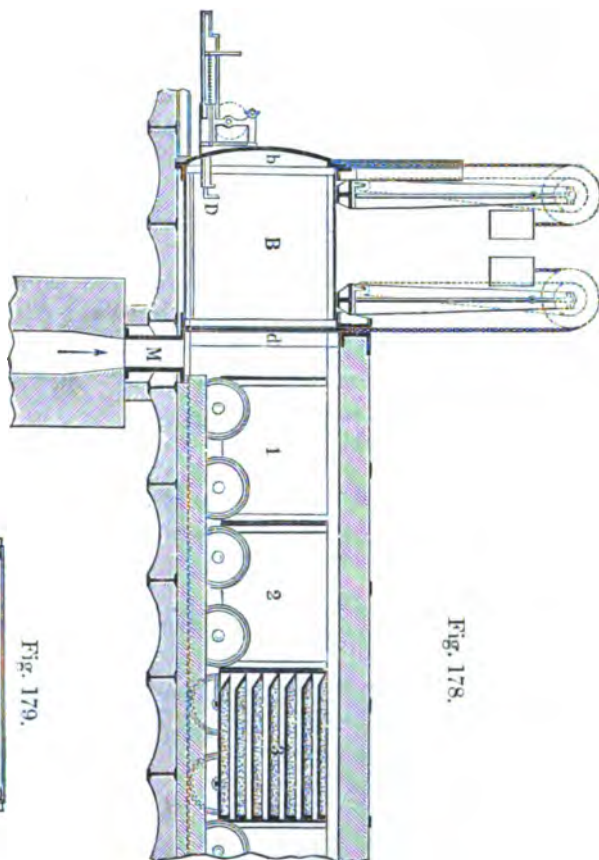


Fig. 178.

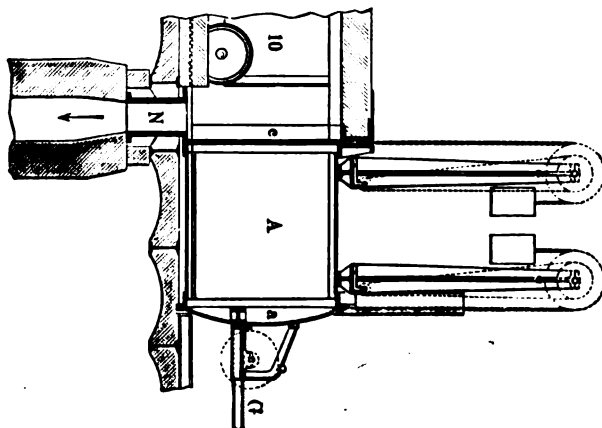
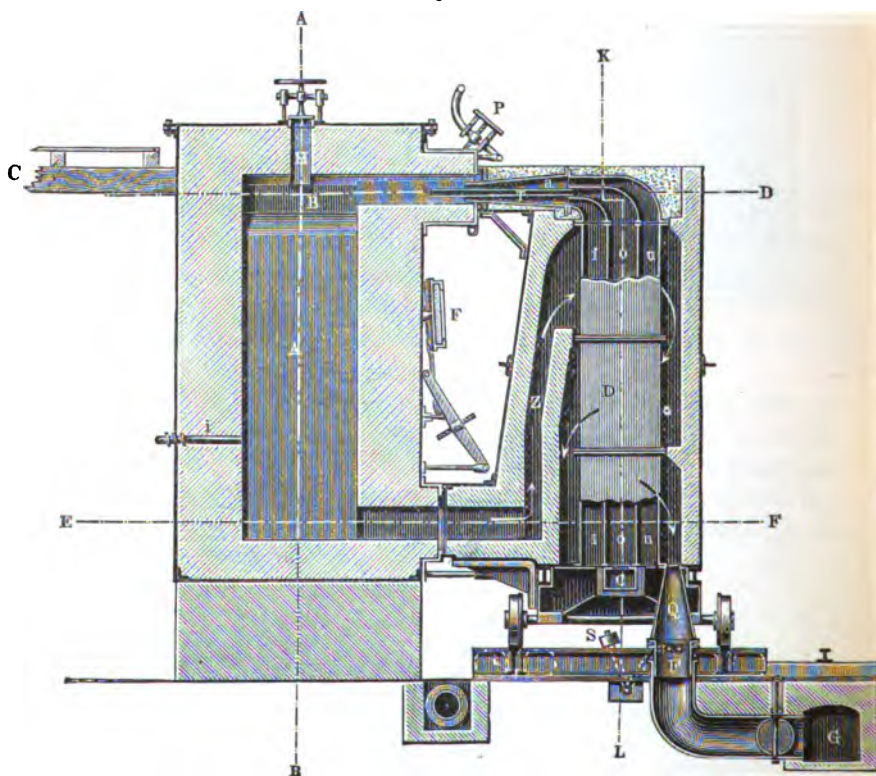


Fig. 179.

**Fifth Operation. *Decomposition of Magnesium Oxychloride.***— This is difficult in consequence of the mass being a bad conductor of heat, so that it could not be brought to a red heat in externally fired retorts, unless by an enormous expenditure of fuel; nor could the heating be performed as quickly as is required for a successful operation.

The furnace constructed for the object in question is the most ingenious part of the whole apparatus. It borrows its principles partly from the ancient baker's oven and partly from Cowper's hot-blast stoves, but it presents a very peculiar solution of this difficult problem. Fig. 180 shows a vertical section of the furnace proper and of the movable burners; fig. 181 a horizontal section, on the top from C to D, at the bottom from E to F in fig. 180. In both the movable burner is shown in the position which it

Fig. 180.



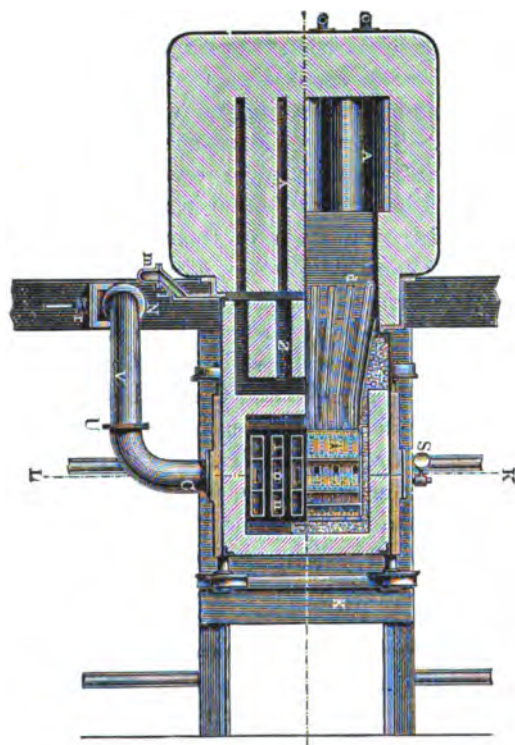


Fig. 181.

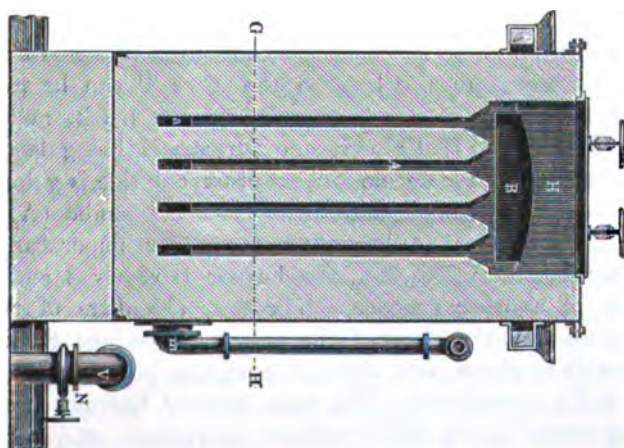


Fig. 182.

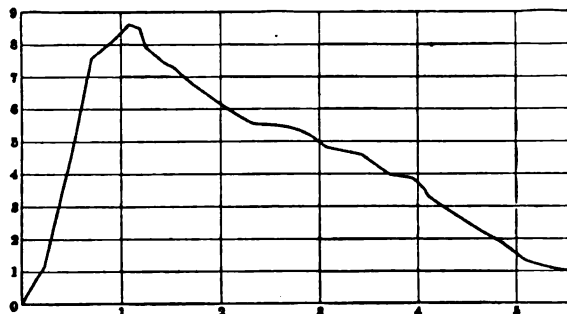
occupies during the operation of heating-up. Fig. 182 shows a vertical section of the furnace proper. A, A, A, A are four narrow decomposing chambers, having very thick walls. The upper extremity of each opens into the combustion-chamber B, and the lower extremity communicates with the four horizontal channels *a, a, a, a*. The movable regenerator burner, fig. 180, consists of a system of cast-iron pipes, contained in an envelope of masonry, encased with strongly-bound iron plates. The pipes are of rectangular section, and each of them is divided by vertical partitions into three compartments, *i, o, u*. The central compartments *o, o* convey gaseous fuel into the combination-chamber, the side compartments *i, u* convey air into the same. The producer gas is supplied by the main upon which is the valve N, fig. 181, from which it passes by pipes V and C into the compartments *o, o*, in which it ascends, and issues through the small pipes *d, d* into the combustion-chamber B. The air for combustion enters at the bottom of the compartments *i* and *u*, and at the top issues through the wide flat pipe T into B. The small pipes *d, d*, pass through T and project a little outside. The pipe V is fixed to the stationary main pipe; it can be, by U, quickly connected or disconnected with the pipe C fixed on the movable burner.

The flame formed in B enters the narrow chambers A, A at the top, leaves them below at *a, a*, and passes upwards through Z Z into the burner, where it plays round the rectangular cast-iron pipes and passes away by P into the flue G. Thus the producer-gas and the air receive a preliminary heating. P communicates by Q with the flue by which the products of combustion are taken away; by means of the lever S the piece P can be raised or lowered. The burner stands on rails upon a truck, and can be moved sideways, so that always one furnace is being heated up, while in the other the decomposition of oxychloride is going on.

The work is carried on as follows :—The four chambers A, A, A, A of one of the furnaces are brought to the proper temperature; then, after charging the valves, &c., the burner is removed and placed in front of another furnace. The four chambers of the first furnace are quickly charged through the openings H, H, with oxychloride in pieces, and through openings in the door F air is drawn in by an aspirator. The mass quickly becomes heated by the heat stored in the thick walls of the furnace, and a mixture of gases and vapours escapes from the chambers, containing both Cl and HCl; it passes through *a, a* into the space at F, and from

there through *l* into pipe *m*. When the decomposition has sufficiently advanced, the current of air is shut off, door F is opened, the oxide is drawn out and removed through *a, a*. Now the lid is again put on H, F is opened, and the burner is brought back again.

Fig. 183.



The curve, fig. 183, shows the rate of the evolution of chlorine. The time after charging is marked on the horizontal lines, the percentage of chloride in the gas (by volume) on the vertical lines. With operations of 408 to 420 kil., 15 to 19 per cent. of the chlorine introduced remained in the residue; 42.4 to 45.2 per cent. was evolved in the free state, and 38.1 to 40.0 per cent. as HCl. The gases contained *in maximo* 6.25 to 7.78 vol. per cent. of chlorine.

Dewar thinks that at first very much steam is given off, which forms and carries away a corresponding quantity of HCl. Then anhydrous  $\text{MgCl}_2$  and  $\text{MgO}$  remains, and now the oxygen forms  $\text{MgO}$  and free chlorine. The reaction is, however, reversible, so that from  $\text{MgO}$  and  $\text{Cl}_2$ ,  $\text{MgCl}_2$  and  $\text{O}$  may be regenerated.

[Kingzett (Journ. Soc. Chem. Ind. 1888, p. 286) has shown it to be probable that in the Péchiney-Weldon process not merely the reaction assumed by the inventors,  $\text{MgCl}_2 + \text{O} = \text{MgO} + \text{Cl}_2$ , is going on, but that the  $\text{MgO}$  behaves towards the HCl as a catalytic substance, and favours the oxidation of HCl by atmospheric oxygen in a similar way to the copper salt in the Deacon process. The free chlorine is not merely formed from the entirely dry magnesium oxychloride, but also from the HCl formed in the decomposition of the oxychloride containing 20 per cent. of water.]

The gases are drawn off by a two-bell aspirator, plunging into a concentrated solution of calcium chloride in which chlorine is almost insoluble. The aspirator acts only behind the condensing-apparatus, which consists of:—1. A glass-tube refrigerator. 2. A number of stoneware bombonnes (receivers). 3. An ordinary coke condenser. The glass-tube refrigerator has been specially devised for quickly and thoroughly cooling hot dilute gases. It consists of a stone tower, two opposite sides of which are perforated with many holes. Through each two of these holes a glass tube passes in a slightly inclined position. The ends of the tubes project from the tower; those on the lower side are connected by india-rubber tubes with a water-pipe, those on the upper side, also by india-rubber tubing, with gutters. Cold water constantly passes through, and owing to the inclined position of the tubes always keeps them full, so that they do not crack by the heat of the gases. This apparatus is shown in figs. 184 and 185. The hot gas enters

Fig. 184.

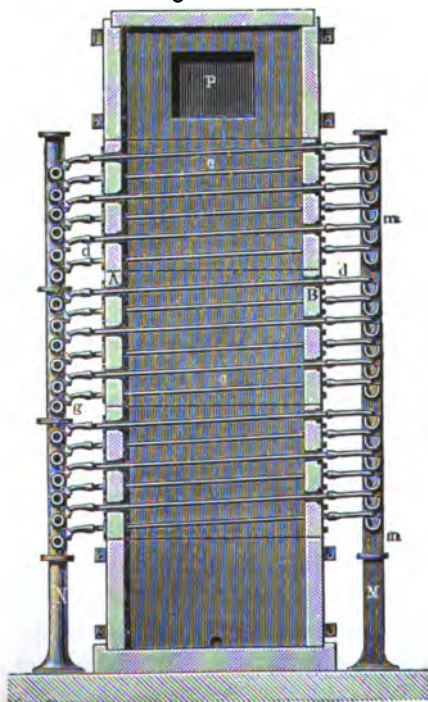
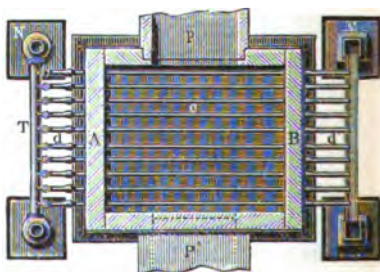


Fig. 185.





at the top, plays round the glass tubes and issues at the bottom; the condensing liquid runs away at the bottom. If a glass tube breaks, this is at once perceived by the fact that no water issues from it into the open gutter; it can then be exchanged in a moment without disturbing the work.

From the cooler the gas passes into the bombonnes and then into the coke-condenser. The mixed acid shows  $18^{\circ}$  Tw., but it could be made stronger by suitable means. The chlorine freed from HCl now goes into the aspirator and then to the place where it is to be utilized.

The magnesia coming from the decomposing furnaces is cooled in a vessel provided with a mechanical agitator and a water-jacket, and is then sifted in a revolving sieve. About  $\frac{3}{4}$  passes through the sieve as a powder, containing hardly 4 per cent. Cl;  $\frac{1}{4}$  remains on the sieve. The latter is slightly modified oxychloride, which is at once mixed with oxychloride from the fourth operation and worked up again. When working a Stassfurt product, from 100 parts  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , a residue of 20 parts MgO will be obtained; the 4 per cent. Cl retained by this amount is only 2·3 per cent. of the original substance.

The total chlorine entering into the process as  $\text{MgCl}_2$  is accounted for as follows:—

Mechanically lost at the different stages...	5·00	
„ „ in drying.....	6·27	
	————	11·27 per cent.
Re-introduced into the process with the		
residue .....	13·30	
As condensed HCl .....	35·29	
	————	48·59 „
Obtained in the free state .....	40·14	„
	————	
		100·00

These 40·14 free chlorine have been obtained from  $100 - 48·59 = 51·41$  chlorine; hence, when allowing for that which returns into the process, 78 per cent. of the chlorine is utilized.

A better result than the above might be expected if the temperature of the furnace could be raised much above that which has been hitherto obtained ( $1000^{\circ}$  C.). The furnace at Salindres consists of two parts of nine chambers, each 3 metres high, 1 metre

long, and 0.08 metre wide. Such a unit should produce per 24 hours 1000 kil. free chlorine, viz., six operations at 170 kil. Cl each. The present heating arrangements do not permit more than four operations, but with better heating five operations should be attained.

We shall not repeat here the calculations given in the original. It may suffice to say that according to Péchiney's statement the apparatus then working at Salindres was capable of producing 1000 kil. chlorine at 209 frs. (without counting the cost of HCl or  $MgCl_2$ ), and that he believed he could make 1000 kil. chlorine in a larger or better constructed apparatus for 118 frs., of which 48 frs. is for coals. Under English conditions Dewar believed he was able to reduce this to 94 frs., that is, equal to the cost of ordinary Weldon chlorine, without counting the HCl. The advantage of the new process would be that instead of the 33 per cent. utilized in the old Weldon process, 78 or 80 per cent. of the chlorine of HCl would be available. This would save per ton of Cl two tons of HCl, equal (according to Dewar) to £5 12s. Altogether, taking £2 16s. as the value of 1 ton of HCl, 1 ton of chlorine would cost by the old Weldon process £13 1s., by the Péchiney-Weldon process £7 9s., and at Stassfurt, where the value of magnesium chloride is *nil*, only £5 (even without allowing anything for the magnesia obtained in the process). He concludes that the chlorine industry would emigrate to Stassfurt. The cost of plant per ton of chlorine made in 24 hours is estimated by Péchiney = 120,000 frs., that is twice as much as an old Weldon plant. [Probably the plant would cost much more, and the repairs for that complicated and extensive apparatus must also be rather heavy.]

There seems to be no doubt that the Péchiney-Weldon process, applied to *hydrochloric* acid, cannot compete with the Deacon process, as improved by Hasenclever. The latter requires much less complicated and costly apparatus, and obtains much more chlorine, viz. 88 per cent., allowing for the recovered hydrochloric acid. The best proof of this is that the process has been stopped at Salindres itself. Weldon, Péchiney, and Dewar had themselves declared that the proper locality for working it is at Stassfurt; but none of the manufacturers there had seen their way to adopt it, although they carefully looked into it. The Péchiney-Weldon process is at work at Szakowa, in Austrian Poland, where



it is applied to magnesium chloride, prepared from the  $\text{CaCl}_2$  of the ammonia-soda manufacture by the Schaffner-Helbig treatment with  $\text{MgO}$  and  $\text{CO}_2$  (Vol. II. p. 860). At that factory only chlorate of potash is made, 8 cwt. per 24 hours (Zsch. f. angew. Chem. 1892, p. 709).

F. Fischer (Zsch. f. angew. Chem. 1888, p. 549) calculates the theoretical requirement of heat for producing a kilogram-molecule (35.5 kil.) of chlorine by the Péchiney-Weldon process as follows:—

1. Chemical work .....	13,500 cal.
2. Heating the air .....	62,000 „
3. „        magnesia .....	24,400 „
4. „        steam.....	37,900 „
5. „        chlorine and $\text{HCl}$	11,200 „
	<hr/>
	149,000 „

To this must be added the loss by convection and radiation from the brickwork. The cooler has to perform work corresponding to the items No. 2, 4, and 5 = 111,100 calories, which must be taken into account when calculating the cooling-water.

Eschellmann (Chem. Ind. 1889, p. 51) gives an extremely detailed calculation of the theoretical quantities of heat required for the Péchiney-Weldon process; but in spite of its ingenuity it has no practical value, as in the end there is a doubt whether in reality six or nine times the theoretical quantity would be consumed (probably far more than even the latter, which Péchiney stated as one which he *hoped* to attain, but which he practically exceeded by 50 per cent.). Eschellmann certainly predicts a bright future for the process; he calculates the cost of a ton of bleaching-power at Stassfurt = £3 10s., without allowing for the value of 5 cwt. of magnesia; and the cost of a ton of chlorate of potash, when combining the Muspratt-Eschellmann magnesia process with working up the  $\text{MgCl}_2$  liquor formed therein by the Péchiney-Weldon process, at £26. Both these figures would represent enormous profits in comparison with the prices current in 1889 and at the present day; but nobody has seen his way to the adoption of the process, and this will be all the less likely since the development of electrolysis.

Evidently practical men have had no confidence in the calculations of Péchiney, Eschellmann, and others (comp. Nahnsen,

Zsch. f. angew. Chem. 1889, p. 673); they have also been deterred by the cost and complication of the plant. But for all that the Péchiney-Weldon process is most interesting, and may possibly come to the front again; at all events it deserves, by the ingenious construction of the apparatus, which is a model for other cases, the somewhat lengthened treatment I have given it here, which is rather out of proportion to its present practical importance.

The following processes show more or less analogy with the Péchiney-Weldon process:—

Wilson (Engl. pat. 3098, 1885) evaporates a solution of magnesium chloride up to the point that a sample solidifies on cooling, and then runs it into a furnace, on the hearth of which the residue from a former operation is still left; this absorbs the liquor, whereupon the whole is heated in a current of air, in order to produce chlorine, or of steam, to produce HCl.

The Vereinigte chemische Fabriken at Leopoldshall (Germ. pat. 43500) employ a mechanical arrangement for moulding the magnesium oxychloride.

Gamble (Engl. pat. 11581, 1888) decomposes the oxychloride in a revolving furnace. Mühlig (Germ. pat. 51183) employs a special gas-furnace for the same purpose.

Lyte and Tatters (Engl. pat. 17217, 1889) prepare in different ways a specially porous magnesium oxychloride; for preparing anhydrous  $MgCl_2$ , they employ the ammonium double salt.

Ramdohr, Blumenthal, & Co. (Germ. pat. 19259) mix a solution of  $MgCl_2$ , concentrated to 40° or 50° Baumé, with from 4 to 10 per cent. of magnesite, and heat it to a red heat in a current of air.

Nithack (Germ. pat. 30742) brings the hot concentrated solution in contact with heated brick surfaces in the state of spray.

Lyte (Engl. pat. 6333, 1890) describes a fresh method for preparing magnesium oxychloride.

#### *Chlorine from Anhydrous Magnesium Chloride.*

The above-mentioned inventions endeavour to avoid the difficulty caused by the splitting off of HCl in the working up of hydrated magnesium chloride by forming an oxychloride. Another series of inventions refers to the formation of anhydrous  $MgCl_2$ , under such circumstances that little or no HCl is split off, and that then by means of air MgO and Cl can be produced.

The Kaliwerke Aschersleben (Germ. pat. 32338) treat crystallized  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in a vacuum at a temperature never reaching the fusing-point. Other patents (Nos. 34404 and 36916) describe special vacuum apparatus for this object.

Konther (Germ. pat. 41351) believes that the decomposition of magnesium chloride can be promoted by calcium chloride.

Vogt (Germ. pat. 37083) describes a combination of a "shelf-burner," exactly similar to the Malétra burner, Vol. I. p. 252, with a horizontal revolving iron cylinder; the mass, thickened in the latter, is put into the furnace and gradually worked from the top shelf down to the bottom. By injecting air, free from  $\text{CO}_2$ , and heated in recuperator chambers, chlorine is produced.

The furnaces of Heinzerling and Schmid (Germ. pat. 41996, 47197, 48845; Engl. pat. 13648, 1888) are more intended for the production of  $\text{HCl}$ ; they are described in Vol. II. p. 435.

Solvay (Engl. pat. 4417, 1889) heats crystallized  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in a current of air not above  $120^\circ$ , by which 80 per cent. of the water is removed without fusion or expulsion of  $\text{Cl}$  or  $\text{HCl}$  (?).

It is preferable to mix it first with half its weight of anhydrous  $\text{MgCl}_2$ , in which case it is possible to heat as high as  $300^\circ$  or  $400^\circ$  without fusion. The air is first dried by chloride of calcium or sulphuric acid, and then carries along all the steam, so that anhydrous  $\text{MgCl}_2$  remains. This is now treated in the fused state with hot air, and gives up its chlorine. Special apparatus is described for this purpose. This treatment in the fused state is supposed to avoid the drawbacks in treating  $\text{MgCl}_2$  in the pulverulent state.

Schlösing (Engl. pat. 11821, 1887) concentrates a solution of  $\text{MgCl}_2$  in open pans to a temperature of  $165^\circ$  or  $170^\circ$ , and heats further in a special furnace, with stirring, until the mass becomes granular, and contains only 30 per cent. water; 3 to 5 per cent. of the chlorine escape as  $\text{HCl}$ , which is condensed. On further heating from without to a red heat, he obtains a mixture of  $\text{MgO}$  and  $\text{MgCl}_2$ , containing from 40 to 50 per cent.  $\text{Cl}$ , which is mixed with 20 to 30 per cent.  $\text{MgO}$ , moulded into bricks, and heated in a current of air at a dark-red heat, which produces a gaseous mixture containing 30 per cent.  $\text{Cl}$  by volume. He employs for this purpose an upright furnace (kiln) with three concentric rings. Between the inner and the middle ring there is a number of

vertical heating-flues, 4 to 6 inches wide; the space between the middle and the outer ring is filled with a network of bricks, serving as a heat recuperator for heating the air. The work is continuous. The moulded bricks already mentioned are heated from without in the central shaft, by means of the small heating-flues; this is done with air, heated in the recuperators, which then enters into the central shaft and here expels chlorine from  $\text{MgCl}_2$ . In order to produce as much anhydrous  $\text{MgCl}_2$  as possible, the atmosphere of the central shaft must be charged with hydrogen-chloride vapour of the highest practicable tension. This produces the desired effect, according to the following account, which I heard from the inventor himself, as communicated in *Zsch. f. angew. Chem.* 1889, p. 699.

If the heating is effected in a current of air, according to the laws of dissociation a mixture of  $\text{HCl}$ , steam, and free  $\text{Cl}$  must escape, and each time a chemical equilibrium must be established corresponding to the partial pressure of the gases, which prevents either of the above three substances being formed to the exclusion of the others. If the latter result is required, the chemical equilibrium in the dissociation of hydrated magnesium chloride must be shifted, which can be done in various ways. If, for instance, hydrated magnesium chloride is heated in a current of steam, it is possible to expel the whole of the  $\text{HCl}$  and to retain pure  $\text{MgO}$  in the residue (this is the rationale of the process of Heinzerling and Schmid, Vol. II. p. 373). On the other hand, the heating may be performed in a current of dry  $\text{HCl}$ ; then only the water of the hydrated magnesium chloride is expelled, and ultimately anhydrous  $\text{MgCl}_2$  remains behind. [This was shown to be the case long before by Dumas; special, unpublished experiments have been made on this subject by H. Gall.] If once anhydrous  $\text{MgCl}_2$  has been obtained, the preparation of chlorine can be most easily effected by a current of dry air at a dark-red heat, say  $450^\circ$ ; the oxygen is quantitatively exchanged for chlorine, and a mixture of 30 to 35 per cent.  $\text{Cl}$  with 70 to 65 per cent.  $\text{N}$  is obtained:  $\text{MgCl}_2 + \text{O} = \text{MgO} + \text{Cl}_2$ . The point in question is, turning the drying of the hydrated magnesium chloride into a practical operation. Schlösing's patent of 1887 endeavours to effect this by separately condensing the first escaping mixture, which contains much steam and little  $\text{HCl}$ , neutralizing it with  $\text{MgO}$ , and re-employing the  $\text{MgCl}_2$  formed. In the second stage

principally HCl escapes, which is not accompanied by a sufficient quantity of water to be condensed to liquid acid; a great deal of HCl remains in the state of gas, which is drawn away by a pump and re-injected into the front part of the retort. By this circulation of HCl a sufficient tension of this gas is produced to obtain a residue testing from 60 to 80 per cent.  $\text{MgCl}_2$  and from 40 to 20 per cent.  $\text{MgO}$ . This particular mixture is advantageous, because the  $\text{MgO}$  prevents the fusion of the  $\text{MgCl}_2$ , which would stop the gases from penetrating through. Altogether the process must be carried on in such a way that the mass always remains porous, in which respect Schlösing follows the lead of the Péchiney-Weldon process.

Eschellmann (Chem. Ind. 1889, p. 31) justly points out that in this process at least 37 per cent. of the chlorine comes back as HCl, and that the drying of  $\text{MgCl}_2$  in HCl gas must be a costly and troublesome operation.

Schlösing's process was to be carried out by Messrs. Bell Bros. at Middlesborough, but nothing more has been published about it. Probably nothing has come of it, for Schlösing in 1891 took out fresh patents (Nos. 11469 and 11470) for a new furnace, with a detailed description of the process, which does not seem to have been carried out as yet. The solution of  $\text{MgCl}_2$  is to be boiled down in circular flat-bottomed iron pans with mechanical agitators by means of gaseous fuel, until it has turned granular; the heating is to be continued in three superposed cast-iron cylinders to a dark-red heat, passing HCl through in the above described manner, the mass being gradually moved from one end of the retort to the other. Here it is turned into white anhydrous  $\text{MgCl}_2$ , which is now charged into horizontal gas-retorts, in which perforated plates are placed a little above the bottom. The  $\text{MgCl}_2$  is placed upon these in a layer of 8 inches thickness; air, heated to a dark-red heat, is introduced in the top of the retort, and the chlorine formed, which, owing to its specific gravity, sinks to the bottom, is carried away from underneath the false bottom.

The most important attempts at producing chlorine (and hydrochloric acid) at Stassfurt have been made by the Salzbergwerk Neu-Stassfurt. They seem to have been so far successful that a certain, but not a large, quantity of those bodies is really manufactured there. Owing to the great secrecy with

which this is treated, we must simply refer to the patents. These can be mentioned only very briefly, as they contain descriptions of a host of furnaces, most of which could not have answered their purpose. Evidently no new principle comes into play; the reactions



are always employed, and the task can only be that of devising and testing more perfect technical means for carrying them out on a large scale.

The first of the German patents of the above-named firm (No. 36673) describes reverberatory furnaces with an inclined hearth, also in connection with kilns. No. 46215 describes muffle-furnaces, several of which are superposed, but can be worked independently. No. 47043 shows a muffle-furnace from which the  $\text{MgCl}_2$  falls into an upright retort, where the mass is withdrawn at the bottom. The top of the muffles is built up in a peculiar way with tubular bricks, through which the heating gases pass. No. 54830 shows hearths, arranged in tiers, so as to keep the less decomposed mass separate from that which is further advanced. No. 51209 describes retorts made of fire-bricks. No. 55461 prescribes cooling the hot acid gases by salts containing water of crystallization, which in fusing absorb heat like the chlorides of calcium, magnesium, or strontium.

A notice in Chem. Ind. 1892, p. 468, states that one of the Stassfurt works where magnesium chloride was decomposed had relinquished the process; the other factory did not make chlorine, but hydrochloric acid, which was worked up by the Weldon process.

## V. CHLORINE FROM AMMONIUM CHLORIDE.

In the ammonia-soda manufacture all the chlorine of the sodium chloride converted into carbonate is changed into ammonium chloride, from which the ammonia up to this day is expelled by lime. Since this transforms the chlorine into the chemically fixed form of calcium chloride, and since the attempts at liberating the chlorine from this, or, by substituting magnesia for lime, from magnesium chloride, have hitherto been economically unsuccessful, it is easy to understand why attempts have been made to treat the ammonium-chloride liquors in a different manner, with the object of utilizing the chlorine.

In all cases the mother liquors of the ammonia-soda manufacture are first deprived of volatile ammonium compounds by systematic heating (p. 106). They then contain, besides  $\text{NH}_4\text{Cl}$ , large quantities of sodium chloride. This must be separated as completely as possible, which can be effected during the boiling-down of the liquor, as the  $\text{NaCl}$  becomes insoluble in the concentrated solution and can be removed by fishing. Some inventors assert that the value of the common salt thus recovered pays the cost of evaporating the liquor; but this does not apply to the majority of localities where ammonia-soda is made, since there the salt, in the form of concentrated brine, has next to no value, and even in the solid state its value is very small.

In Mond's process of decomposing the ammonium-chloride vapour by magnesia, to be described later on, the separation of  $\text{NH}_4\text{Cl}$  from the liquor freed from  $\text{NaCl}$ , is to be effected by freezing-out by the aid of an ice-machine. According to Quincke (Chem. Ind. 1893, p. 11), the temperature must be considerably below  $0^\circ$ , and the crystallized ammonium chloride contains much ammonium bicarbonate, sodium chloride, and sodium bicarbonate, which, however, will not do much harm during the further treatment. The subsequent drying will not cause much difficulty.

Schreib (Chem. Zeit. 1894, p. 1952) points out that as early as 1885 he had patented the first part of Mond's process, consisting in the freezing-out of the ammonium chloride from such liquors. The point in question is not merely the production of cold, but to a great extent also the displacing of the  $\text{NH}_4\text{Cl}$  from its solution by  $\text{NaCl}$ , so that the cooling need not go below  $+4^\circ$ . The liquor, filtered from the ammonium chloride, and containing about 23 per cent.  $\text{NaCl}$  and 6 per cent.  $\text{NH}_4\text{Cl}$ , can be reintroduced at once into the carbonating process. This saves both common salt and the distillation of large quantities of liquor.

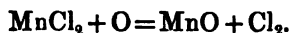
We have already (p. 128) mentioned the processes of Mond, Gilloteaux, and Witt, all of which proposed to expel the chlorine from the  $\text{NH}_4\text{Cl}$  liquor in the shape of  $\text{HCl}$ , but without much practical success. Here we only treat of the processes by which the chlorine is to be obtained from the ammonium chloride in the free state. An indispensable condition for *every* process intended for this object is the complete recovery of the *ammonia*, the value of which far exceeds that of the chlorine, to the same extent as in the ordinary lime process.

Bale (Engl. pat. 14001, 1887) heats ammonium chloride, mixed with manganese oxide,  $Mn_2O_3$ , in a retort. At  $130^\circ$  the ammonia begins to escape, and at  $325^\circ$  has all volatilized. The heating is continued for some time below  $350^\circ$ , passing an indifferent gas over the mass, to expel all moisture. Then the temperature is raised to  $400^\circ$ , and dry hot air is passed through the retort, producing a gas with from 9 to 12 per cent. by volume of chlorine. The residue, after yielding up its chlorine, is again mixed with ammonium chloride and re-utilized. If the ammonium chloride contains sodium chloride, this must be removed from the residue by washing from time to time. According to a new patent (No. 15649, 1889) Bale suspends powdered manganese oxide in fused zinc chloride and introduces ammonium chloride; after the  $NH_3$  has escaped, the last of it being driven out by cold dry air, the  $MnCl_2$  formed is to be decomposed by dry hot air into regenerated manganese oxide and chlorine, thus obtaining a gas which contains from 12 to 20 per cent. chlorine.

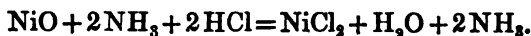
The Verein für chemische Industrie at Mainz (Engl. pat. 3322, 1886) passes the vapours of ammonium chloride over any one of the oxides of manganese at a temperature below red heat. When employing  $MnO$  the reaction is:—



If now hot air is passed over the residue,  $MnO$  and chlorine is obtained:—



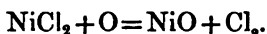
The most persistent efforts for the direct manufacture of chlorine from ammonium chloride have been made by Mond, whose first patents are:—Nos. 65, 66, 1049, 3238, and 8308, all of 1886; comp. p. 564. Ammonium-chloride vapour is brought into contact with oxide of nickel (or oxides of many other metals, which, however, are inferior in this respect to nickel, or salts of those metals with non-volatile acids like silica, phosphoric acid, &c.) at a temperature of  $400^\circ C$ . The chlorine is retained, steam and ammonia are carried further, and the latter is condensed in the usual manner. The reaction is:—



In order to completely expel the ammonia, a chemically inert gas, *e. g.* producer-gas, or the exit-gas from the ammonia-soda process



(principally consisting of nitrogen), is drawn through the apparatus by means of a vacuum-pump. If the chloride thus formed is exposed to the action of steam, heated to  $450^{\circ}$ , NiO is re-formed and the chlorine expelled as HCl. If, however, instead of steam, dry air heated to  $500^{\circ}$  is forced through, free chlorine is formed :—



In both cases the oxide of nickel is regenerated, and the process can be at once started again with fresh  $\text{NH}_4\text{Cl}$  vapour. The NiO therefore remains always in the same place. It is employed in the shape of pumice, impregnated with  $\text{NiCl}_2$ , and then ignited, or in the shape of lumps, moulded by means of cementing substances, with addition of sawdust, and converted into a porous mass by igniting. This contact-substance is placed in iron retorts, lined with thin fire-bricks, a number of which are set in a furnace at an angle of  $30^{\circ}$ . During the first stage, when the vapour of  $\text{NH}_4\text{Cl}$  passes through, the heat is kept at  $400^{\circ}$ , during the second, when air passes through, at from  $500^{\circ}$  to  $550^{\circ}$ . The air is previously well dried by sulphuric acid or chloride of calcium, and is then heated to  $500^{\circ}$  in a hot-blast stove. By this process a gas with 5 to 7 per cent. chlorine by volume is obtained.

As iron is attacked by the vapours and gases, it is preferable to employ iron enamelled inside or lined with clay, graphite, gypsum, or barytes, or to place a thin fire-clay retort within the iron retort, filling up the intermediate space with iron filings, or to employ iron coated inside with nickel, and so forth.

At first Mond mentioned a process in which the retorts are filled half with nickel oxide, half with solid ammonium chloride, the latter being volatilized in the retort itself. But he seems soon to have resorted to generating the  $\text{NH}_4\text{Cl}$  vapour in a special vessel, and only then passing it through the NiO. The volatilization of ammonium chloride on a large scale is rather difficult, because the substance does not melt; the vapours surround the solid particles and do not allow the heat to penetrate from without. To obviate this drawback, patent No. 10955, 1887, prescribes introducing the solid ammonium chloride gradually into a bath of fused chloride of zinc, which is placed in a cast-iron pan, lined with earthenware, or in a nickel pot; or the volatilization is to take place in a vacuum, or in a current of inert gas, which lessens the tension of the  $\text{NH}_4\text{Cl}$  vapour. Further, as the contact-substance, after the

$\text{NH}_3$  is expelled, obstinately retains water, which acts injuriously at the next stage, the treatment with inert gases is to be continued after the expulsion of the ammonia, as long as  $\text{HCl}$  escapes, which is conveyed into a condensing-apparatus. The gases obtained later on by treatment with hot air, which always contain some  $\text{HCl}$  along with the chlorine, are passed through metallic oxides, which are kept between  $100^\circ$  and  $500^\circ$ , and which retain all the  $\text{HCl}$ , but no chlorine. When afterwards treated with hot air, they equally yield up the chlorine in the free state. It is convenient to employ three superposed retorts: in the top retort the material is brought into contact with the gases which are formed in the bottom retort by contact with the air, and which at the top give up their  $\text{HCl}$  and yield pure chlorine. From the top retort the mass is moved down to the middle one, where it is treated with  $\text{NH}_4\text{Cl}$  vapour; and at last down to the bottom retort, where it is treated with air.

Evidently the nickel-oxide process did not answer in working it out, for Mond returned to *magnesia*, which had been employed by so many previous inventors. It is already mentioned in his former patents as a contact-substance, but is there declared to be inferior to nickel oxide. Here the drawback is encountered that the magnesium chloride or oxychloride, left after expelling the  $\text{NH}_3$ , retains a good deal of water, which in the subsequent treatment with hot air re-converts from 20 to 40 per cent. of the  $\text{Cl}$  into  $\text{HCl}$ . A better solution of this difficulty than by patent No. 10955, of 1887, seems to have been found in that taken out by Mond and Eschellmann, No. 17273, 1887. To the finely ground magnesia from 5 to 10 per cent. sodium or potassium chloride is added and the mixture is worked into a paste, with addition of from 5 to 10 per cent. china-clay; the mass is moulded into bricks or lumps and dried. It is then exposed to the  $\text{NH}_4\text{Cl}$  vapours in a Deacon apparatus at a temperature of  $400^\circ$ : as soon as small quantities of  $\text{NH}_4\text{Cl}$  pass through undecomposed, the supply of vapour is cut off; there is then no water left in the mass. If now dry air is passed through at between  $450^\circ$  and  $500^\circ$ , chlorine almost free from  $\text{HCl}$  is obtained. The alkaline chloride remains unchanged, and the mass can continually serve over again. When employing hydrochloric acid, its vapour mixed with air in the same proportion as in the Deacon process may be passed through at between  $450^\circ$  and  $550^\circ$ , and a continuous manufacture of chlorine may be thus established.

Mond's patent No. 10957, 1887, describes an apparatus, probably intended for the above purpose, but generally applicable to the treatment of solid substances with gases, or even to the roasting of pyrites and similar purposes. The substance is employed in thin layers, is constantly turned over and is exposed to the current of gases coming from the opposite direction. Revolving cylinders do not fulfil this object completely, because the gas passes through them in a compact mass, and the contact with the solid substance is not sufficiently intimate. This is better effected by the apparatus shown in figs. 186 to 189. Fig. 186 is a longitudinal section, fig. 187 a cross-section through  $x-x$ , fig. 188 a cross-section through  $y-y$ , fig. 189 a view from behind. The two concentric cylinders, A and B, enclose an annular space C. They are both rotated by the spur-wheel  $D^1$ , fixed on A, which rests on the rollers  $D^1$ . The solid substance enters in the annular space at E and leaves by  $E^1$  by means of the conveying-screws  $e$  and  $e^1$ , moved by the pulleys  $d$ . The gas enters in the opposite direction into F by the hollow shaft  $e^2$  and leaves at  $F^1$  by the hollow shaft  $e^3$ , as indicated by the arrows; the stuffing-boxes G  $G^1$  provide the necessary seclusion from the outer air. In order to lengthen the passage of the gas, the screw-flange H is fixed on the outer cylinder A; the turning over of the solid substance is effected by the ribs or buckets I, running parallel with the axis, which always lift the mass a little and drop it again. Similar ribs J are attached to the inner cylinder; the substance lifted up by I first falls on to J, is carried over to the other side of the cylinder and there falls on to the outer cylinder. The inner cylinder is tightly closed by cover  $b$ . The outer cylinder projects at both ends beyond it and beyond the furnace. In the exit end the radial ribs  $e^1$  are fixed inside and drop the substance into the discharging arrangement  $e^1$  (fig. 186). The apparatus is mounted horizontally or slightly inclined.

A further patent, No. 2160, 1889, prescribes lining the vessels in which the ammonium chloride is volatilized with antimony, or an alloy containing much antimony, which effectually resists those vapours and is much cheaper than cobalt or nickel; there are also no vapours of metallic chlorides formed in this case. To obviate the drawback caused by the low fusing-point of antimony and its alloys, the evaporating-vessel is to be filled with a bath of melted chloride of zinc, reaching above the fire line, the upper portion of the vessel being cooled below the melting temperature of antimony,

but kept sufficiently hot to prevent any solid  $\text{NH}_4\text{Cl}$  from depositing there. A temperature of  $350^\circ$  is suitable for this purpose. This apparatus is shown in fig. 190 (p. 616).

Fig. 186.

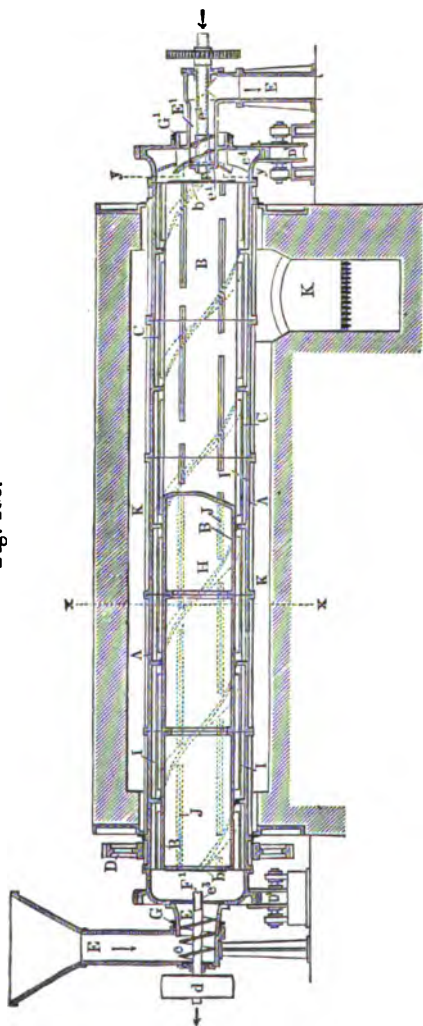


Fig. 189.

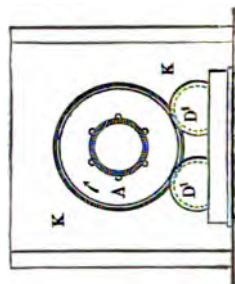
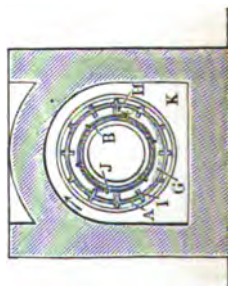


Fig. 188.



Fig. 187.



A somewhat definite idea of the process, arrived at after several years' experiments, seems to be contained in patent No. 2575, 1889, which describes the apparatus as follows:—The vapour of

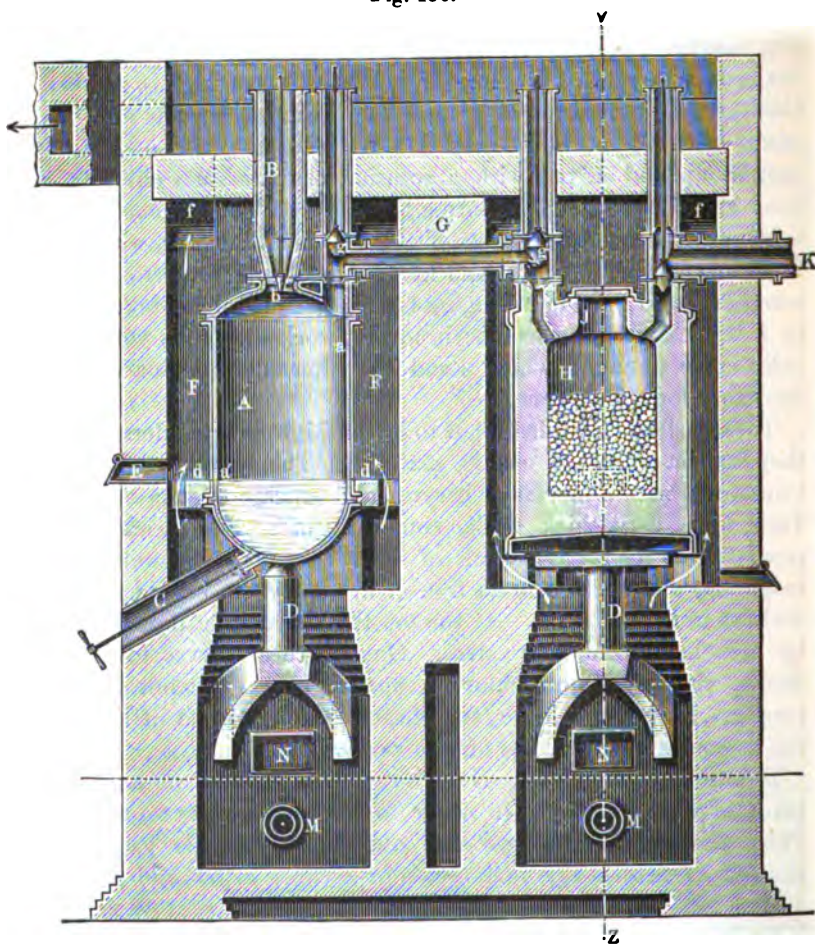
ammonium chloride, produced by a bath of zinc chloride in the above-described cast-iron pan, lined with antimony, is conveyed by cast-iron conduits, lined with antimony or fireclay tiles, kept at  $350^{\circ}$ , into vertical cylinders, filled with the contact-substance. The latter is composed of magnesia, with addition of alkaline chlorides (p. 612), china-clay, and a little lime or calcium chloride. The magnesia should not be too dense; it is preferable when it has been precipitated by lime from a solution of  $\text{MgCl}_2$ , washed, filter-pressed, and dried at a moderate heat. 100 parts of it are mixed with 75 of china-clay and 6 quicklime, the mixture is ground up and mixed with a solution of potassium chloride of spec. grav. 1.085 to 1.000 into a thin paste. This is moulded by mechanical means into pellets of about  $\frac{1}{4}$ -inch diameter, which are dried and ignited at a dark-red heat. The drying is performed on a endless band passing through a hot flue; the igniting takes place in a vertical iron retort continuously worked. Thus very hard pellets are obtained which stand the alternate chlorination and oxidation for a long time.

These pellets are piled up 6 to 8 feet high in cylinders, where they rest on a layer of coarser material. The cylinders consist of brickwork, with a mortar of barytes and silicate-of-soda solution. They have very thick walls, consisting of several brick rings, separated by bad conductors of heat (for instance, anhydrous magnesia) and encased in an iron shell. They can be heated from without in case of need. At the top they have inlet pipes, closed by nickel or stoneware valves. One of these serves for introducing the ammonium-chloride vapour; others for hot or cold inert gas, for hot or cold air, superheated steam, &c. A little above the bottom are the outlets for the various gases.

Before introducing the  $\text{NH}_4\text{Cl}$  vapour, a current of hot inert gases is passed through, in order to heat the pellets up to  $350^{\circ}$ . Then this gas is shut off and ammonium-chloride vapour is allowed to enter; the ammonia now escapes below and is conducted into an absorbing-apparatus. When sufficient vapour of  $\text{NH}_4\text{Cl}$  has passed through, it is shut off and inert gas, heated to  $500^{\circ}$  or  $550^{\circ}$ , is admitted, which sweeps out the ammonia and is equally conveyed to the absorbing-apparatus. When no more  $\text{NH}_3$  is found in the gases,  $\text{HCl}$  appears in its stead, and the gas is then directed into another absorbing-apparatus. When no more  $\text{HCl}$  is evolved, the pellets will have attained  $500^{\circ}$  or  $550^{\circ}$ ; at all events

they must be brought up to that temperature by passing hot inert gases through. These gases should be as free as possible from oxygen and steam, lest they should themselves act on the  $\text{MgCl}_2$ .

Fig. 190.

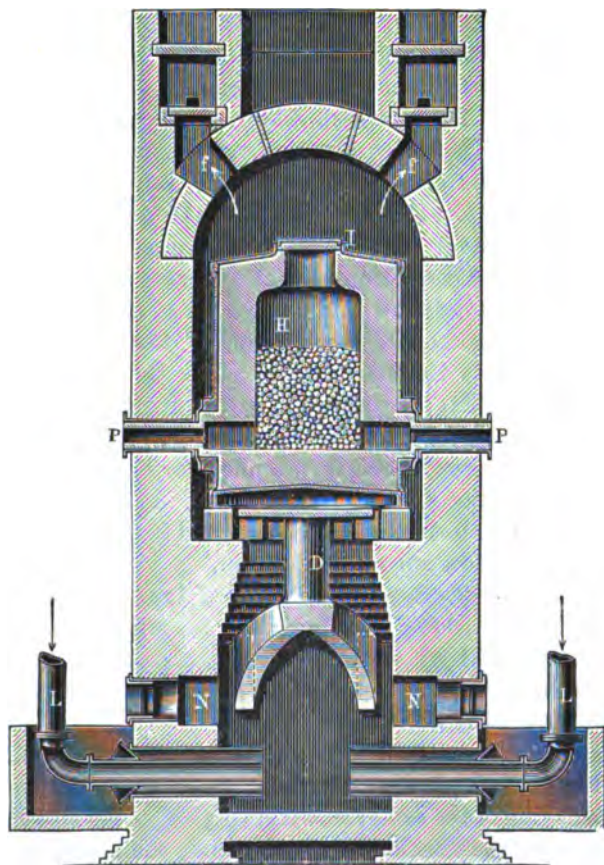


The best gases for this purpose are good lime-kiln gases, or those escaping at the top of the carbonating towers of the ammonia-soda works, after careful drying by sulphuric acid.

When the proper temperature has been reached the inert gas is shut off and a current of air is introduced, previously dried by

sulphuric acid and heated by a Cowper's hot-blast stove to from  $800^{\circ}$  to  $1000^{\circ}$  C.; this quickly decomposes the  $\text{MgCl}_2$ . At the bottom a gas escapes, containing from 7 to 10 per cent.  $\text{Cl}$ , and

Fig. 191.



practically free from  $\text{HCl}$ , if the operation has been carefully conducted, so that it can be directly conveyed into a Deacon's bleaching-powder chamber (p. 404). Eventually the gas becomes too poor in chlorine; it is then conveyed again into a Cowper stove, heated to  $800^{\circ}$  or  $1000^{\circ}$ , and passed through another cylinder charged with  $\text{MgCl}_2$ .

After driving out the chlorine, a current of cold air or inert gas



is passed through to reduce the temperature to  $400^{\circ}$ . The air, which takes up some heat here, is further heated in a Cowper stove and employed as above. When the temperature is lowered, fresh  $\text{NH}_4\text{Cl}$  vapour is introduced, and so forth.

Figs. 190 and 191 show the apparatus in two sections (fig. 191 along the line YZ in fig. 190). A is the apparatus mentioned above (p. 613), filled with zinc chloride, for volatilizing the ammonium chloride; it consists of a cast-iron pan with an antimony lining *a*. The zinc-chloride bath *a'* reaches up to the annular brick-wall *d*, which supports the sides and keeps back the fuel-gas. The solid ammonium chloride is introduced through B, by means of valve *b*. C is an outlet-pipe, D brick supports, *d* side stays, E inlet-pipe for air, for cooling the upper space, *f* flues for the fuel-gas, G the connexion with the decomposer H, with valves *g* and *g'*. If *g'* stands low and *g* high, A is connected with the atmosphere; if *g* occupies the low and *g'* the high position, H communicates with the atmosphere. H is the decomposer filled with magnesia pellets; I the manhole for introducing the pellets; J exit for chlorine; P exit for ammonia; K inlet for air or inert gases; L inlet for producer-gas, intended for heating-up; M inlet for air; N manholes.

If, instead of chlorine, hydrochloric acid is to be produced, the hot air is replaced by superheated steam.

Patent No. 19812, 1892, prescribes purifying the ammoniacal gas from  $\text{NH}_4\text{Cl}$  by washing with hot water or milk of lime, and the chlorine from  $\text{HCl}$  by washing with calcium-chloride solution. The mode in which the solution of  $\text{NH}_4\text{Cl}$  and that of  $\text{HCl}$  in  $\text{CaCl}_2$  are utilized is well known.

A writer in Chem. Ind. 1892, p. 466, points out the difficulties involved by Mond's process: Freezing-out the ammonium chloride; complete drying of the same; complete drying of the air; the action on the vessels; the dilution of the chlorine; the action of the  $\text{HCl}$  on the apparatus; the great consumption of fuel for heating the decomposer at widely different temperatures; the small durability of the magnesia pellets; the greater cost of  $\text{CO}_2$  in comparison with the ammonia-soda process, as the lime cannot be utilized *in loco*; greater losses of ammonia; high wages and frequent repairs.

Quincke (*cod. loco*, 1893, p. 10) objects to some details of this criticism, but he himself draws attention to the following points:—



Very great consumption of fuel; difficulty of exactly regulating the temperature and keeping the various gas-conduits tight; great cost of plant and repairs; necessity of frequently renewing the zinc chloride and the magnesia pellets. His final judgment is also that the process cannot pay for plant and working expenses, although at that time 6 tons of bleaching-powder per 24 hours were said to be manufactured at Winnington.

A reply in *Chem. Ind.* 1893, p. 63, still further elucidates the drawbacks of the process. This seems to be contradicted by Hasenclever's statement (*ibid.* p. 372), according to which the daily production had increased to 15 tons bleaching-powder about the end of 1893. But this gives us no clue to the real cost of that bleaching-powder.

The thermochemical data of Mond's process are calculated by Townsend (*Engineering*, March 24, 1893) as follows:—The solution of ammonium chloride from the ammonia-soda process contains 20 per cent.  $\text{NN}_4\text{Cl}$ ; hence four times its weight of water must be evaporated. (Instead of evaporation, Mond freezes out the  $\text{NH}_4\text{Cl}$ , but this will hardly cost less, looking at the unavoidable losses.) The  $\text{NH}_4\text{Cl}$  must now be dried, volatilized, and heated to  $350^\circ$ . This requires theoretically for a kilogram equivalent:—

	Calories.
Evaporating $53.5 \times 4\text{H}_2\text{O}$ ( $53.5 \times 4 \times 537$ ) .....	114,918
Decomposing $53.5 \text{NH}_4\text{Cl}$ .....	41,900
Heating $17 \text{NH}_3$ from $100^\circ$ to $350^\circ$ ( $17 \times 0.5084 \times 250$ )...	2,160
Heating $36.5 \text{HCl}$ from $100^\circ$ to $350^\circ$ ( $36.5 \times 0.194 \times 250$ )	1,770
	<hr/>
	160,748
Deduct for the solidification of $\text{NH}_4\text{Cl}$ .....	3,880
	<hr/>
	156,868

On the (practically quite impossible) supposition that all the chlorine is converted into the free state, 71 Cl is obtained to 40 MgO; 16 O come into action, and  $18 \text{H}_2\text{O}$  is formed. Hence  $16 \text{O} = 80$  air must be heated to  $1000^\circ$ . This requires the following amounts of heat:—

	Calories.
80 kil. air heated to 1000° ( $80 \times 0.2375 \times 1000$ ).....	19,000
40 „ MgO „ from 350° to 1000° ( $40 \times 0.244 \times 650$ )...	6,344
Heat absorbed by the substances mixed with MgO.....	5,000
35.5 x 2 Cl heated from 350° to 1000° ( $71 \times 0.12 \times 650$ )...	5,538
18 steam heated from 350° to 1000° ( $18 \times 0.48 \times 650$ ) ...	5,600
	<hr/> 41,482

This total refers to  $\text{Cl}_2$ ; hence half of it, =20,741 calories, must be added to the above, which brings it up to 177,609 calories for the kilogram equivalent of chlorine. This should be contrasted with the Deacon process, which gives a theoretical surplus of heat in the chemical reaction (p. 378), and where the heating only rises to 500°.

Bale (Journ. Soc. Chem. Ind. 1894, p. 200) mixes dry, powdered ammonium chloride with magnesia, and first, by heating from without to 200° C., drives out all the  $\text{NH}_3$ ; then, by means of superheated steam at 450° to 500°, all the  $\text{HCl}$  from the  $\text{MgCl}_2$ . The residue is used in the same apparatus for decomposing  $\text{NH}_4\text{Cl}$ . The apparatus consists of several superposed retorts, in the shape of shallow cylinders with internal agitating-gear. Two-thirds of the ammonium chloride are introduced in a dry state, in a thin layer, the last third is run in as a concentrated solution, which forms lumps with the dry mass. The escaping  $\text{HCl}$  gas is dried by strong sulphuric acid, heated up in a Cowper stove, and passed through manganese oxide contained in a Deacon decomposer, where  $\frac{1}{3}$  of the  $\text{HCl}$  is evolved as undiluted chlorine; the  $\text{MnCl}_2$  formed yields the other  $\frac{2}{3}$  chlorine in a dilute state to a current of dry hot air, and is reconverted into  $\text{Mn}_2\text{O}_3$ .

Greenwood (Engl. pat. 11655, 1894) treats the solution of ammonium chloride with *oxide of zinc*, distils the ammonia off, and decomposes the zinc chloride by electrolysis into free chlorine and free zinc. The  $\text{ZnO}$  is to be obtained from calamine by roasting, and the  $\text{CO}_2$  then given off is to be employed in the ammonia-soda process.

## FOURTH BOOK.

# PREPARATION OF ALKALIS, CHLORINE, AND CHLORATES BY ELECTROLYSIS.

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## CHAPTER XXIV.

### HISTORY; THEORIES; GENERAL NOTES.

IN 1800 Cruikshank noticed that, on electrolyzing a solution of common salt, caustic soda was formed at the negative pole. In 1803 Berzelius and Hisinger confirmed this observation. About the same time Davy recognized that during the electrolysis of potassium sulphate, caustic potash is formed at the negative, and sulphuric acid at the positive pole.

A long time elapsed before these observations were utilized in the actual manufacture of chemicals. In the first edition of this work, published in 1880, altogether 15 lines are devoted to the electrolytic manufacture of alkali, concluding as follows:—"Such processes could in any case only become useful if the electricity required for decomposing a molecule of common salt could be generated with the expenditure of less coal than we require in the ordinary process, which undoubtedly is not the case."

It will hardly be denied that this remark was perfectly justified at that time, as well as the brief treatment of the matter. As late as 1888 Dr. Hurter occupied practically the same standpoint (*Journ. Soc. Chem. Ind.* 1888, pp. 722 to 725). At this day, however, the state of the case is widely different, and we must, in a Treatise on the Manufacture of Alkali and Chlorine, devote considerable space to electrolysis.

The electrolytic processes occupy a peculiar position in the alkali industry. In most other cases alkali occupies the most prominent place. The ammonia-soda process is practically to this day exclusively a process for the manufacture of soda. This was equally the case with the Leblanc process in its infancy; as late as 1880 there were factories in England and France where the hydrochloric acid formed in the manufacture of saltcake was almost entirely lost, either in the shape of gas or in that of a very dilute liquid. The pressure of competition has certainly put an end to such culpable waste, and consequently the hydrochloric acid, or the bleaching-powder manufactured from it, sometimes plays a more important financial part in the Leblanc process than the soda itself; but, *quantitatively*, in that process the soda is still the chief factor, whether it is sold as soda-ash or as caustic. Up to a short time ago the Leblanc works produced two or three tons of soda-ash, or its equivalent of caustic, for every ton of bleaching-powder producible from the whole of the hydrochloric acid generated. Since the Deacon process has been completely worked out, the yield of bleaching-powder has certainly been largely increased, and a number of new processes (none of which has been permanently introduced on a large scale) promise even more than the above. Nevertheless, the last statistics obtainable on that point in England (unfortunately since 1887 no statistics as to the actual manufacture of alkali and bleaching-powder have been published) show that for each ton of bleaching-powder (including its equivalent of chlorate of potash) there was produced a quantity of alkali equivalent to three tons of soda-ash, or to  $2\frac{1}{2}$  tons of 60-per-cent. caustic soda. This is explained by the fact that the great bulk of all bleaching-powder is still made by the Weldon process.

The case is quite different with electrolysis. Here 58.5 parts of common salt are split up into 23 sodium and 35.5 chlorine. Expressing this in terms of the commercial products, we obtain for 55 tons of the strongest soda-ash or 40 tons of the strongest caustic soda about 100 tons of bleaching-powder. In many cases the aim of electrolysis is not to produce alkali, but bleaching-liquor or chlorate of potash, the temporarily formed caustic alkali returning over and over again into the cycle of manufacture. In these cases the electrolysis is not in any sense a process for the manufacture of alkali; but even in those, more numerous, cases

where the aim is to produce caustic or carbonated soda, these articles, although important factors in respect of the profits to be realized, are certainly of only secondary importance, both financially and quantitatively. In electrolysis the preparation of chlorine can under no circumstances be considered a mere adjunct to that of alkali, in the sense in which this was formerly, and to a certain extent is still, valid for the Leblanc process, but rather *vice versé*. For this reason, and also on account of the intimate connexion between electrolytic processes which produce alkali and those which do not, we cannot treat of electrolysis either among alkali processes or among chlorine processes, but we must describe it in a separate section by itself.

We cannot of course give here a general treatise on electro-chemistry, and we must refer the reader to the text-books of physics and physical chemistry, as well as to monographic treatises on this matter. It seems, however, appropriate to supply the reader with such data as he will require for practical work, and to accompany these with brief theoretical explanations. We must also briefly describe some important experimental researches referring specifically to the electrolysis of chlorides.

#### EXPLANATION OF THE PRINCIPAL PROPERTIES OF THE ELECTRIC CURRENT.

The nature of the electric current is best understood by comparing it with a current of water conducted down hill in a closed pipe with a certain gradient. The work producible by this mass of water at the lower end of the pipe will depend, first, upon the quantity of molecules of water present; secondly, upon the pressure under which they issue from the pipe, that is upon the gradients. We will call the former, expressed in kilograms,  $i$ , and the difference of level between the upper and lower end of the pipe, expressed in metres,  $e$ . If we assume that we have not a store of water at our disposal, placed by nature at the higher of the two levels, but that we must raise its quantity of water from the lower to the higher level, we must evidently expend a quantity of work  $= i e$ , expressed in metre-kilograms, or  $= \frac{e}{76}$ , expressed in

metrical horse-powers (an English H.P. is  $=1.014$  metrical horse-power).

Evidently we shall not recover all this work, expended upon raising the water to the higher level, on allowing it to flow back through the pipe, for we must suffer a certain loss of energy through friction on the walls of the pipe and through the mutual friction of the particles of water against one another. This amount of energy, which we will call  $w$ , is, of course, not annihilated, but it is transformed into heat, which in nearly every practical case is lost for our purposes by being radiated into space, although there is no theoretical impossibility in utilizing that heat, produced by friction, in special cases, where fuel is not available. It is clear without further explanation that the loss of energy by friction must be in proportion to the length of the pipe, and must be smaller in the case of a pipe of larger diameter. It is also evident that pipes of different kind, say with smooth or with rough internal surfaces, must oppose quite different resistances to the current, the width of the pipe remaining the same. The frictional resistance  $w$  must also be much increased, if we choose to divide a certain sectional area of the conduit among several pipes, instead of employing a single larger pipe.

The frictional resistance  $w$  will make itself felt as follows:— In order to produce the flow of a certain quantity of water  $=i$  in the unit of time through the pipe, we must increase the magnitude  $e$ , that is the head of water, by as much as corresponds to the smaller or larger frictional resistance. The magnitude  $i$  is therefore directly proportional to  $e$ , and inversely proportional to  $w$ : if the difference of level  $e$  is a definite amount, the outflowing quantity  $i$  will be less as the frictional resistance  $w$  is greater, and  $i$  will increase with an increase of the difference of level  $e$ .

These considerations allow us to establish the following laws for the above hydrodynamic case:—

1st. The work required for storing up a certain quantity of energy is equal to the product of the *quantity* of water into the *difference of level* (the head of water), or  $=ie$  metre-kilograms.

2nd. The work producible by this quantity of water stored at a higher level, by allowing it to flow downwards through a tube, is directly proportional to  $i$  and  $e$ , but inversely proportional to the resistance  $w$ .

3rd. The quantity of water  $i$  arriving at the bottom is directly proportional to the pressure  $e$ , and inversely proportional to the resistance  $w$ .

All these considerations may be applied to *the electric current*. The quantity of water  $i$  corresponds to the *intensity of the current*  $I$ ; the difference of level, gradient, or pressure  $e$  to the *electromotive force*, the *potential*, or *tension*  $E$ ; the frictional resistance  $w$  to the *electrical resistance*  $W$ . We distinguish an internal resistance produced within the generator of electricity (galvanic cell or dynamo), and an external resistance, existing in the conducting parts, the baths, &c. The *electrical work* is also equal to the product from current-intensity and tension, or  $IE$ . The relations between the above-mentioned magnitudes are expressed by Ohm's law :  $I = \frac{E}{W}$ ; that is, the current-intensity is directly proportional to the electromotive force and inversely proportional to the resistance.  $W$  is, of course, the sum total of the resistances within the dynamo, the conductive parts, and the baths.

It is evident that the electric current, just like a current of water, can be treated in different ways, viz., either by subdividing its *quantity* among various channels, that is, allowing the current-intensity to act simultaneously upon several baths; or by not utilizing the total *gradient* all at once, but interrupting this in various places and utilizing at the end of each fraction that part of the total gradient which constitutes the difference of gradient or "tension" existing between each two fractions of the gradient; or else by producing both kinds of subdivision at the same time. The first method is styled working with *parallel poles*; the second, working *in series*.

*Conduction of Electricity*.—Bodies which do not offer any considerable resistance to the passage of electricity are called *conductors*; those which offer so much resistance that the current is hardly traceable are *non-conductors* or *insulators*.

There are two classes of conductors. *Conductors of the first class* are those elementary substances which allow the current to pass through without undergoing any change: to these belong the metals and graphite (plumbago). The current performs in them work, manifested in the shape of heat, proportional to the time, the resistance, and the square of the current-intensity, that

is  $= t w i^2$  (Joule's law). The *conductors of the second class*, or *electrolytes*, are substances in which, apart from the work of producing heat, molecular work is produced by the splitting up of chemical compounds into their constituents. These constituents may be either elementary atoms or groups of atoms, and are called *ions* (see below).

The resistance, according to our former observations, is directly proportional to the length and inversely proportional to the sectional area of the conductor; it is greatly influenced by the concentration and temperature.

The electric resistance in the case of conductors of the first class *increases* with an increase of temperature; in the case of metals almost always according to the formula:

$$K_t = K_0 (1 - 0.0037t),$$

where  $K$  is the specific conductivity, and  $t$  the temperature. In the case of conductors of the second class, the resistance *decreases* with an increase of temperature, and that in a much higher ratio than the increase in the previous case. Thus the specific conductivity of a solution of 24.9 per cent. NaCl in water increases according to the formula:

$$K_t = 0.00001254 (1 + 0.0307t + 0.000142t^2).$$

For a 26-per-cent. solution of NaCl Kohlrausch gives this formula:

$$K = 0.00002015 + 0.00000045 (t - 18^\circ).$$

For conductors of the first class, the usual unit chosen is the resistance of silver, taken = 100. Most of the other metals, except copper, are greatly inferior to silver in this respect; but the statements of different authors are not at all concordant, evidently owing to the various degrees of purity of the metals tested. The graphitic modifications of carbon are also conductors (while diamond and charcoal are not), but their conductivity increases with the temperature.

The conductivity for heat mostly runs exactly parallel to that for electricity:—

Silver .....	100
Copper .....	77
Gold .....	55
Zinc .....	27



Brass .....	22
Iron .....	14
Tin .....	12
Platinum .....	10
Lead .....	8
Mercury .....	1.6
Bismuth .....	1.8
Graphite .....	0.07 to 0.40
Gas carbon .....	0.04
Bunsen's carbon .....	0.003

The electrical resistance of a copper wire of 1 millim. diameter (0.785 square millim. section) per metre is 0.022 ohm; at 2 millim. diameter (3.14 sq. millim.) = 0.0056 ohm; at 3 millim. diameter (7.07 sq. millim.) = 0.0025 ohm, and so on. 1 ohm is equal to the resistance of a column of mercury 1.063 metres long and of a section of 1 square millimetre at 0° C.; this is equal to the resistance of 45 metres (147.5 feet) copper wire of a diameter of 1 millimetre (= 0.039 inch), or the resistance of 100 metres (328 feet) of iron wire of a diameter of 4 millimetres (= 0.157 inch).

As regards the resistance of conductors of the second class, we quote the *specific resistances* of a number of electrolytes, for columns of 1 square decimetre section and 1 decimetre long, expressed in ohms. In the case of solutions, we also quote the decrease of percentage of resistance for 1° C.

For other lengths of  $a$  decimetres and sections of  $q$  square decimetres the resistance is  $w = \frac{a}{q}$ .

*Fused Salts.* (Fr. Braun.)

Potassium nitrate .....	0.1451;	taken at 342°
Sodium nitrate .....	0.0822	„ 315
Potassium carbonate .....	0.4388	„ 1150
Sodium carbonate .....	0.439 to 0.46	„ 920
Sodium sulphate .....	0.2564	„ 1280
Sodium chloride .....	0.1089	„ 960
Lead chloride .....	0.0373	„ 580
Zinc chloride .....	10.98	fused.

*Solutions. (F. Kohlrausch.)*

		Spec. Gravity. At 18°.	Spec. Resistance. ohm.	Decrease for 1° C. per cent.
Potassium chloride, 5%	.....	1.0308	1.4626	2.02
"	10	1.0638	0.7422	1.89
"	15	1.0978	0.4994	1.80
"	20	1.1335	0.3767	1.69
"	25	1.1408	0.3590	1.67
Sodium chloride, 5%	.....	1.0345	1.5022	2.18
"	10	1.0707	0.8334	2.15
"	15	1.1087	0.6146	2.13
"	20	1.1477	0.5155	2.17
"	25	1.1898	0.4726	2.28
"	28	1.1982	0.4691	2.31
"	28.4	1.2014	0.4680	2.34
Calcium chloride, 5%	.....	1.0409	1.5697	2.14
"	10	1.0852	0.8841	2.07
"	15	1.1311	0.6705	2.03
"	20	1.1794	0.5838	2.01
"	25	1.2306	0.5666	2.05
"	30	1.2841	0.6086	2.17
"	35	1.3420	0.7388	2.37
Magnesium chloride, 5%	.....	1.0416	1.4764	2.23
"	10	1.0859	0.8942	2.21
"	20	1.1764	0.7196	2.38
"	30	1.2779	0.9520	2.84
"	34	1.3201	1.3158	3.19
Potassium chlorate, 5%	.....	1.0316	2.742	2.12
		At 15°.		
Potassium carbonate, 5%	.....	1.0449	1.793	2.22
"	10	1.0919	0.9696	2.13
"	20	1.1920	0.5702	2.11
"	30	1.3002	0.4531	2.20
"	40	1.4170	0.4645	2.47
"	50	1.5728	0.6856	3.20
Sodium carbonate, 5%	.....	1.0511	2.235	2.53
"	10	1.1044	1.431	2.72
"	15	1.1590	1.206	2.95
		At 15°.		
Potassium hydroxide, 4.2%	.....	1.0382	0.6873	1.88
"	8.4	1.0777	0.3697	1.87
"	12.6	1.1177	0.2675	1.89
"	16.8	1.1588	0.2209	1.94
"	21.0	1.2088	0.1972	2.00
"	25.2	1.2430	0.1864	2.10
"	29.4	1.3008	0.1854	2.22
"	33.6	1.3332	0.1929	2.37
"	37.8	1.3803	0.2104	2.58
"	42.0	1.4296	0.2392	2.84

		Spec. Gravity. At 18°.	Spec. Resistance. ohm.	Decrease for 1° C. per cent.
Sodium hydroxide,	2.5% .....	1.0280	0.9258	1.95
"	5 .....	1.0568	0.5113	2.02
"	10 .....	1.1131	0.3223	2.18
"	15 .....	1.1700	0.2908	2.50
"	20 .....	1.2262	0.3018	3.01
"	25 .....	1.2823	0.3710	3.70
"	30 .....	1.3374	0.4986	4.50
"	35 .....	1.3907	0.6695	5.54
"	40 .....	1.4421	0.8871	6.52
"	42 .....	1.4625	0.9481	6.95

According to Ohm's law, the electrical resistance consumes a corresponding quantity of electromotive force. It is therefore necessary to keep it as low as possible, in order to produce the greatest amount of electrical work. As regards external conductors, which consist of metal (mostly copper), this is easily attained by enlarging the section. In the present case the internal resistance of the baths is much greater, and this must be lessened as far as possible by suitable concentration and by heating the electrolyte (comp. above); also by decreasing the current-density, that is, enlarging the surface of the electrodes up to the maximum allowed by the process, and by bringing the electrodes as close to each other as possible; the latter certainly, in the absence of a diaphragm, not beyond the point where a short circuit might be caused. A considerable portion of the internal resistance is usually caused by the diaphragm (membrane) dividing the anode chamber from the cathode chamber (see below).

The electrolytes conduct the current whilst undergoing a *decomposition*; the constituents which separate are called *ions*. The electro-negative ion is separated at the place where the positive electricity enters into the bath; the electro-positive ion where the negative electricity enters. The parts introducing the electricity are called *electrodes*; that forming the positive pole is called the *anode*, and the (electro-negative) ion separating there the *anion*; the negative pole is formed by the *cathode*, and the positive ion separating there is the *cation*.

The ions may be elementary substances—*e. g.* chlorine as anion; sodium, copper, &c. as cations,—or else they are groups of elements not capable of existing in the free state, and splitting up within the liquor by secondary reactions. Thus the anion  $\text{SO}_4$  reacts at once with water and forms  $\text{SO}_4\text{H}_2$ , with separation of

free oxygen, which is hence not formed by the electrolysis itself, but by a secondary reaction. In the same way the hydrogen, so frequently disengaged at the cathode in the reaction here referred to, is not primarily formed by electrolysis, but, *e.g.*, by the action of the sodium, formed as cation, on water. Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , splits up into Na and the combination  $\text{NaCO}_3$ , not capable of existing by itself; the sodium at the cathode, acting on water, yields  $\text{NaOH}$  and free  $\text{H}$ ; the  $\text{NaCO}_3$  at the anode, with water,  $2\text{NaHCO}_3$  and free  $\text{O}$ . Sodium bicarbonate itself in electrolysis splits up into Na and the acid group  $\text{HCO}_3$ ; the latter at the anode yields carbon dioxide and oxygen :



*Theory of Electrolytic Dissociation.*—According to the now very generally accepted theory of Arrhenius, based principally upon former researches by Clausius, only such liquids conduct the electric current in which the chemical compounds are at least partially dissociated into their ions, and that exclusively by the motions of these ions, which motions constitute the current. Hence the conductivity, *cæteris paribus*, is proportional to the number and the mobility of the free ions. The mobility, that is the velocity, is the sum of the separate velocities of the anion and cation, which are entirely independent of each other, and are merely dependent upon the frictional resistance of the solvent against the moving ion. At a certain temperature, at a certain gradient of the current, and in a certain solvent the velocity of an ion is entirely a function of its nature, and it is just as much a determinate constant as its atomic weight, its colour, and so forth. The velocity expressed in  $\frac{1}{1000}$  millimetre, with a gradient of 1 volt per millimetre, in aqueous solutions at  $25^\circ\text{C}$ ., is as follows :—

+  
H, 325.

—  
OH, 167.

Metals, 40 to 70.

Anorganic acid radicles, 35 to 75.

Organic ions, 15 to 70.

According to this theory any substance can exist as an ion only on condition of being able to receive and retain an electric charge, positive or negative, corresponding to its valency or capacity of charge. When a salt dissociates on dissolving, the metal becomes positively, the acid radicle negatively electrical.

Certain substances, among them the metals, can enter into solution only if they are capable of receiving positive electric charges. Metals of high dissolving-pressure, *e. g.* zinc, acquire that charge from ions already dissolved; they deprive them thus of their own electric charges. But as ions without charge cannot remain ions, those which are deprived of their charge must pass out of the state of solution; according to circumstances, we then notice the precipitation of a metal or the evolution of hydrogen. Similar phenomena are noticed if we immerse within an electrolyte at least two different conductors of the first class and continually charge them, one with positive, the other with negative electricity. In this case, at the first point the carriers of negative electricity or anions (*e. g.* acid radicles), at the other point the carriers of positive electricity or cations (hydrogen and the metals) yield up their charges and separate out in the molecular state, unless they enter into further reaction with constituents of the solution or with the electrodes. In all cases the transportation of electricity, that is the conduction of current in conductors of the second class, cannot be imagined without movement, that is migration of ions, the cations migrating to the cathode, the anions to the anode.

*Electrical Units of Measure.*—The International Congress of Electricians, held in 1881 in Paris, established the following units, on the strength of deductions not necessary to repeat here:—

The unit of *current-intensity* is the *ampère* (A). It is that constant amount of current which separates from an aqueous solution of silver nitrate 0.001118 gram silver per second, or, according to Faraday's law, in the case of other substances in the same way 0.010386 times the milligram equivalent.

The practical unit of the quantity of current is the *coulomb* (Cb), that is, the amount furnished by a constant current of 1 ampère during 1 second.

The unit of *resistance* is the ohm ( $\Omega$ ), that is, the resistance of a mercurial column, 1.063 metres long and 1 sq. millimetre section, at 0° C. (The units formerly used are the Siemens unit=0.944 ohm, and the B.A. unit=0.989 ohm.)

The unit of the *electromotive force* or *tension* (voltage) is found by measuring the difference of potential at the ends of a resistance=1  $\Omega$ , if a current=1 A flows through the latter; it has been called 1 *volt* (V). The electromotive force of a Daniell's battery=1.12 volt.

The electrical *energy*, like every other, is composed of two factors, the quantity (intensity) and the tension; its unit is therefore the *volt-ampère* (VA) or *watt*. Expressed in mechanical work it is  $= \frac{1}{9.81} = 0.102$  metre-kilogram or  $\frac{1}{736}$  of a metrical ( $\frac{1}{745}$  of an English) horse-power. Calculating its thermal effect from the mechanical equivalent of heat (1 h.u. = 425 metre-kilograms), 1 watt is = 0.00024 large calory, or more accurately 0.24104 gram-calory.

The electrical *work* is expressed in watts per second or hour, &c. The English Board of Trade unit is 1 kilowatt (=1000 watts) per hour.

The above amount of 0.24104 calory, the heat-equivalent of a watt, is actually manifested as heat, if the electric current cannot produce any electrical work, but merely heat. Inversely we require 4.164 watts per second to produce 1 gram-calory.

The relation between these factors of energy and the resistance is represented by Ohm's law:—

$$A = \frac{V}{\Omega}.$$

*The electrical measuring-instruments*, voltmeters and ampère-meters, are now always of that kind which indicates the voltage and amperage directly on a dial. They should be procured from a thoroughly reliable firm, and tested from time to time in a physical laboratory.

#### *Calculation of the Current-Intensity.*

Faraday's electrolytic law, discovered in 1833, in the form given to it by Kohlrausch, is as follows:—"The same amount of current decomposes in the same time the same number of electrochemical molecules"; or else "Each electrochemical molecule requires for its decomposition the same quantity of electricity or intensity of current." For "electrochemical molecule" we may say "valency." We understand thus that currents of equal strength decompose in the same time  $n$  molecules NaCl, but only  $\frac{n}{2}$  molecules  $\text{Na}_2\text{SO}_4$ , or  $\text{CuSO}_4$ , or  $\text{CaCl}_2$ ; also, that from cuprous chloride,  $\text{Cu}_2\text{Cl}_2$ , twice as much metallic copper is separated than from cupric chloride,  $\text{CuCl}_2$ .

Consequently, according to Faraday's law, the electrolytic

decomposing work is a function of the *current-intensity*, which is now universally expressed in ampères (A), and of the *chemical equivalent*, that is the molecular weight, divided by the valency of the element in question. In order to find the real amount of work done, we must first multiply by a constant, amounting for a second to 0.010386 milligram\*, or for an hour to 0.03739 gram. This leads to the subjoined *electrochemical equivalents*; that is, the weights (in grams) theoretically separated per hour (or per 24 hours) by a current of 1 ampère, or else formed by secondary reactions (taking into account that in the formation of chlorates 6 equivalents are used, viz. :



	Grams per ampère in 1 hour.	Grams per ampère in 24 hours.
Chlorine .....	1.3236	31.766
Sodium.....	0.8600	20.640
Potassium .....	1.4582	34.997
Sodium hydrate .....	1.4956	35.894
Sodium carbonate .....	1.9817	47.561
Potassium hydrate .....	2.0938	50.251
Potassium carbonate ...	2.5799	61.918
Sodium chlorate .....	0.6630	15.912
Potassium chlorate .....	0.7627	18.305
Hydrogen .....	0.0374	0.898
Oxygen.....	0.2992	7.184

Of this theoretical decomposing work it is possible to realize, with somewhat rational plant, at least about 80 to 85 per cent. in electrolyzing sodium chloride into chlorine and caustic soda, or 66 per cent. in preparing chlorates.

The causes of the discrepancy between the theoretical and the practically available electrolytical work of the current are various. In the electrolysis of aqueous solutions unavoidable secondary reactions occur (p. 629), in the case of NaCl especially the formation of hypochlorite, of chlorate, or of both. By the application of good diaphragms and in other ways these secondary reactions

\* Sometimes other values are given to this constant, ranging from 0.01035 to 0.010411.

may be lessened, but never entirely done away with; and they naturally become more and more pronounced the further the conversion of NaCl into NaOH proceeds. In the electrolytic preparation of chlorates the secondary reactions are still more troublesome, since here oxygen is split off by the electrolysis of hypochlorite, perhaps also of chlorate.

Another cause of the incomplete efficiency of the current in decomposing NaCl is this: that as soon as NaOH, NaClO<sub>2</sub>, &c. has been formed, the current is not merely conducted by the NaCl, but also by the NaOH &c. A third cause is the "migration of ions" (p. 630). The two last-named phenomena have been frequently investigated, *e. g.* by Hurter ("On Electrolysis": Liverpool Physical Society's Inaugural Address, London, 1893), who is certainly mistaken in assuming that they have been hitherto mostly overlooked. They have led him to the conclusion (long universally held) that the current efficiency continually decreases. It is not worth while to repeat his figures, as they are only valid under his special conditions, and must differ with every other kind of diaphragm, with other temperatures, and altogether with every other special condition of the process. I can affirm, for instance, from my personal observation, that in a most scientifically conducted factory the proper limit for electrolyzing a solution of NaCl was considered to be attained when 25 per cent. of the NaCl had been converted into NaOH, whilst in another factory more than 50 per cent. was transformed, and elsewhere, I am told, even better results are obtained.

The processes in which the solid product of electrolysis does not remain in solution with the electrolyte, but is somehow separated out, avoid the principal causes of loss above pointed out. To this class belong the processes for electrolyzing sodium chloride in the state of fusion, or those in which the cathode is in contact with mercury, which carries away the reduced sodium in the state of an amalgam, without allowing it to be transformed by water into NaOH within the cathode chamber. The same holds good of Lyte's process, in which fused lead chloride is electrolyzed. No secondary reactions, or division of the current among the products of electrolysis, can take place in these cases.



*Decomposing-work within the Electrolyte.*

In order to split up a compound, a molecule, into its ions, we require not merely a certain intensity of current, but also a certain *tension or electromotive force (voltage)*. The current-intensity has a one-sided quantitative action; Faraday's law teaches us that currents of equal strength produce entirely different weights of ions, but always in proportion to their equivalents. We know, however, that we must expend for decomposing a molecule into its constituents the same amount of energy which has been liberated in its formation. This energy, for molecules of a different kind, is not at all proportionate to their equivalents, which alone are apparent in Faraday's law, but equal equivalents of different compounds represent very different quantities of chemical energy, whose measure is afforded by the quantity of *heat* liberated during the formation of each compound from its constituent. This energy must be again brought to bear from without, in the shape of heat or other forms of energy, in order to break up the compound again, and to render to its single constituents once more their former potential energy (chemically speaking, their activity). Since the electric work is composed of current-intensity and tension, and since the current-intensity cannot be proportionate to the combining-energy of the molecules, manifested as "heat of combination," precisely because it is the same for equal equivalents of all compounds, we must seek the second factor of the energy, required for dissolving the chemical bond, exclusively in the *electromotive force*, which hence must be directly proportionate to the "heat of combination." This is also proved by the fact that the heat given out during the passage of a current through a conductor, with currents of equal intensity, that is for an equal number of molecules, depends entirely upon the electromotive force.

We can calculate the necessary amount of electromotive force as follows:—According to p. 632, 4.164 watts is the equivalent of a gram-calory; according to p. 631, 0.010386 milligram, or 0.000010386 gram, is the electrochemical equivalent of a second-ampère for the unit of equivalents (hydrogen). Hence the current-intensity for one gram is:

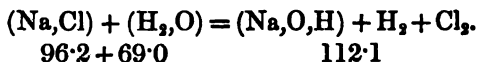
$$\frac{1}{0.000010386} A = 96,283 A.$$

If we denote by  $W$  the heat of formation, including the heat of solution (if any) of a gram-equivalent of any compound in question, and by  $E$  the potential, expressed in volts, we obtain :

$$W = \frac{96,283 E}{4.164} \text{ or } E = \frac{W}{23,112}$$

That is to say, the action of an electromotive force of one volt is equal to the thermochemical equivalent in gram-calories, divided by the constant 23,122, or, if expressed in "large calories," divided by 23.1.

We thus find the electromotive force required for a specific process by dividing the heat of formation, expressed in large calories for each equivalent of the compound in question, by 23.1\*, which signifies the electromotive equivalent of the molecular work required for effecting the decomposition. In the present case, we have principally to do with the splitting up of a solution of sodium chloride into sodium hydrate and chlorine, according to the thermochemical equation :



We must of course deduct from the heat of formation of the electrolyte that of the product; the second system therefore represents 165.2 less 112.1 = 53.1 large calories less than the first, and the transition from the first to the second therefore requires  $\frac{53.1}{23.1} = 2.30$  volts for the molecular work. Exactly the same result holds good for electrolyzing a solution of KCl into KOH and Cl.

These figures are much lower than those to be given below for decomposing the chlorides into the alkaline metals and chlorine. The reason is that the formation, by a secondary reaction, of caustic alkali from an alkaline metal and water is likewise a source of energy, which diminishes the amount of energy in the shape of electricity required for the work of molecular decomposition.

The calculated voltage for decomposing a solution of sodium chloride into Cl and Na (as it occurs, for instance, with a mercury cathode) is much larger, viz. :

\* Berthelot assumes 23.2, others only 23.07, as the thermal equivalent of a volt, as we shall see later on.

$$\frac{96.2}{23.1} = 4.16 \text{ volts;}$$

for potassium chloride into K and Cl:

$$\frac{100.8}{23.1} = 4.36 \text{ volts.}$$

For fused chlorides the thermochemical calculation yields the following figures:—

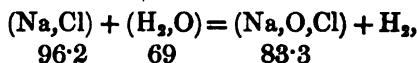
Na,Cl .....	$\frac{97.3}{23.1}$	= 4.21 volts,
K,Cl.....	$\frac{105.0}{23.1}$	= 4.53 „
Ca,Cl <sub>2</sub> .....	$\frac{170.2}{2 \times 23.1}$	= 3.68 „
Pb,Cl <sub>2</sub> .....	$\frac{85.2}{2 \times 23.1}$	= 1.84 „

In these cases, however, the calculated voltage differs widely from that which is practically necessary; the high temperature at which the chlorides have to be kept in fusion is itself a source of energy and greatly diminishes the amount of electrical tension required for the work of decomposition. In other cases the actual voltage is in excess of that calculated.

Apart from this, later investigations of Helmholtz and others have shown that the voltage required for splitting up a chemical compound does not exclusively depend upon the heat set free in the formation of that compound, but that other factors must be taken into consideration, of which we cannot treat here. We may safely omit this, as the deviations caused thereby in the calculations of the voltage from the heat of formation are not generally very considerable. These differences are manifested as "secondary heat" in the decomposing-cell.

In those cases where the products of electrolysis again unite in the bath itself (always with the separation of some secondary product, since otherwise the electrolysis would have no object at all), we must likewise account for the difference of the heats of formation. If we prepare a bleach-liquor by allowing the chlorine formed at the anode to combine with the sodium hydrate formed

at the cathode (the hydrogen being allowed to escape), thus producing sodium hypochlorite, our calculation runs as follows :—



$$\frac{165.2 - 83.3}{23.1} = 3.54 \text{ volts.}$$

We shall mention later on special theoretical and experimental researches on the decomposing-tension of various substances by Nourrisson, Berthelot, and others.

These tensions are only *theoretical minimum values*. In practice very different voltages are required : firstly, owing to the interior resistance of the bath, which in the case of solutions is always much greater than in that of solid (or fused) bodies; especially the nature of the diaphragm separating the anode from the cathode chamber is of great influence in this direction; secondly, owing to *polarization*. Both act in the direction of increasing the actually required voltage. Hence those processes have a great theoretical advantage in which diaphragms &c. can be dispensed with, which is only possible where the products of electrolysis can be prevented from acting upon each other; also those in which no gases are formed in contact with the electrolysis, so that no polarization can ensue.

Nor must we overlook that frequently on the large scale a larger voltage must be employed than on the small scale, since, in order to send a large number of ampères through a given section, where the object is to increase the output, a greater electromotive force than the minimum must be present. According to present experience, we may assume that on the large scale, with good diaphragms, but including the resistance within the bath, a difference of potential = 4 volts is altogether sufficient for electrolyzing solutions of common salt.

Apart from the voltage and amperage, we must not lose sight of the *current-density*, that is the proportion of the surface of the electrodes to the quantity of current sent to them. The best results in every given case are always obtained with a special current-density, varying greatly for different apparatus and processes, and only to be ascertained by experience in each case.

When we have, with a fixed surface of electrodes, attained a

certain limit of current-intensity, we shall not be able to put in more ampères without employing a greater voltage than before. Supposing this limit in a special case to be 500 A, and the voltage to be employed up to that point to be 4 V, we shall not be able to send 1000 A through the same bath without raising the voltage.

If we neglect for the moment the influence of the current-density, the increase of voltage requisite on increasing the quantity of current can be calculated from the following formula, in which  $\Delta P$  denotes the difference of potential,  $I$  the current-intensity,  $E$  the minimum intensity required for splitting up the molecule, together with all other factors remaining constant with changing current-intensities,  $W$  the interior resistance of the bath:—

$$\Delta P \cdot I = E \cdot I + I^2 \cdot W.$$

Dividing this equation by  $I$ , we obtain :

$$\Delta P = E + IW.$$

That is to say, the difference of potential does not increase in the same ratio as the current-intensity, but in a less degree. If  $W$  is a small magnitude in comparison with  $E$ , it will be possible to largely increase the current-intensity without any considerable increase of voltage. This state of the case is, however, modified by the fact that on increasing the current-intensity, without at the same time enlarging the surface of the electrodes, the current-density is also increased, which may cause secondary phenomena, greatly influencing the necessary voltage, nearly always in the direction of increasing it. Thus, in order to force 1000 A, instead of 500, through the bath, the tension may have to be increased from 4 V to 6 or 8 V; and since the work of electrolyzing increases only in proportion to the current-intensity, but is not influenced by the voltage, much more engine-power will have to be expended than is proportionate to the increased electrical effect. But as, according to the above, the current-density is a considerable factor of the voltage, that disproportionate increase of the engine-power required for the extra work to be done can be frequently avoided by enlarging the surface of the anodes or the cathodes, or both. Even in such cases where this is not possible, sometimes a larger than the minimum voltage is employed in order to make the baths work more quickly. This is a matter for special consideration in each case.

The effect of current-density is also shown in the following way :—With very great current-density—that is, powerful currents sent through small electrodes—it may happen that the ions, which are to act upon their surroundings, can do so only partially, because they are not in contact with a sufficiently large surface of the surrounding substance. A similar effect is produced by decreasing the concentration of the electrolyte, in which case the ions may not meet with a sufficient number of molecules to produce the secondary reactions. Both these cases are only valid for *secondary* processes, whilst the primary electrolysis is independent of the size and nature of the electrodes and the concentration of the solution.

As we shall see, most inventors employ *diaphragms* in the electrolysis of aqueous solutions of chlorides, and for a very good reason, viz., to diminish or exclude the secondary reactions. The diaphragms certainly not merely cause a loss of electromotive force by increasing the resistance (p. 625), but are in many cases very fragile. Many inventions refer to this point, as well as to the *anodes*, which are not only continually exposed to the action of chlorine, but suffer even more from the oxygen formed by secondary reactions.

### *Efficiency of the Dynamos.*

Multiplying the voltage by the current-intensity, we obtain *the work to be performed by the dynamo*, which is expressed in “volt-ampères” or “watts” (p. 632). A German or French horse-power (75 metre-kilograms) is equal to 736 watts, an English H.P. (550 foot-pounds) to 746 watts. Instead of horse-power, calculations are frequently expressed in “kilowatts” = 1000 watts (an English “Board of Trade unit” is a kilowatt-hour). With a potential-difference of 4 volts, *e.g.*, a H.P. will furnish  $\frac{746}{4} = 186.5$  A, or, theoretically,  $186.5 \times 1.3236 = 246.83$  grams chlorine per hour, or 5924 grams per 24 hours, or 1777 kilograms in 300 days. This is, however, the efficiency for *electrical* horse-power, that is the work done at the poles of the dynamo, which with large machines is from 7 to 10 per cent. less than the work done by the main shaft, or 15 per cent. less than the indicated H.P. in the steam-cylinder. As value of the latter only 630 watts can be assumed. When expressing the results in kilowatts there is no such uncertainty as to the meaning of the word.

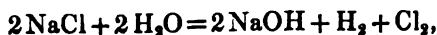
With small machines all conditions are less favourable. Small steam-engines, to begin with, consume much more coal per indicated H.P. than large ones. Good condensing, triple-expanding engines can work with something like 1·8 lb. of coal per H.P. hour, whereas small non-condensing engines consume upwards of 4·8 lb. The former suffer less loss between the cylinder and the main shaft. Large dynamos are also far more efficient than small ones. There is especially a great loss of current efficiency with low-tension dynamos. Therefore high-tension dynamos must be employed, and several baths must be put in series, so that, for instance, a dynamo with 50 volts available tension serves for ten baths with a potential difference of 5 volts each.

Quincke (Chem. Zeit. 1893, p. 654) discourses on the utilization of energy when transformed into the electric current. With the very best steam-engines, consuming only 5·5 kilog. steam per H.P. hour, there is a loss in the steam-boiler of 16 per cent., in the steam-engine of 82 per cent., and in the dynamo of 8 per cent. of the energy introduced. Still this is up to this day the only practically available source of electricity [?]. The dry gas-battery of Mond and Langer (plaster-of-Paris slabs, impregnated with dilute sulphuric acid, covered on both sides with platinum-foil, coated with platinum-black, whilst on one side hydrogen, on the other oxygen, is carried along) has not been practically successful. [Whether the battery of Borchers, Zschr. f. angew. Chem. 1895, p. 26, or others will solve this problem must be left to the future. At present, beyond any doubt, *water-power*, with direct coupling of the dynamo on the turbine, is the cheapest source of electricity.]

*Special Scientific Investigations on the Electrolysis of Chlorides.*

The older researches in this direction do not now present much interest, and will be mentioned only by title: Lidoff and Tisch-riomiroff (Chem. Centralbl. 1882, xiii. p. 747); Naudin and Bidet (Bull. Soc. Chem. 1883, xl. p. 2); Jurisch (Chem. Ind. 1888, p. 100).

Hurter (Journ. Soc. Chem. Ind. 1888, p. 722) admits that the endothermic reaction



demanding for 58.5 grms. NaCl 53,060 heat-units, can be produced by electricity at ordinary temperatures, and that in this lies one advantage of electricity, as well as in the circumstance that by transforming heat into mechanical work wider ranges of temperature can be employed than in the direct application of heat. But compared with our mechanical powers the molecular forces are very large, and it therefore requires very large plant to do comparatively little work. It takes a current of 1000 ampères day and night for three years to produce one ton of hydrogen or its equivalent of any other substance. [That means, *e.g.*, 35.5 tons of chlorine or 100 tons of bleaching-powder.] Moreover, although well-constructed dynamos now change 90 per cent. of the available horse-power into electricity, yet far more electricity than can be calculated from theory is necessary for overcoming the resistances, &c. Taking the cost of a H.P. hour =  $\frac{1}{4}$ d., and assuming that 20 per cent. is lost in transforming mechanical energy into electric currents, and, again, 50 per cent. in changing current into molecular work, Hurter arrives at an amount of £4 as the cost of decomposing one ton of salt into chlorine and a solution of salt containing caustic soda, whereas the Leblanc process sells the whole of the products from one ton of salt for less than £6.

Another drawback is the great loss by resistance in porous diaphragms, which may amount to 0.01 or even 0.1 ohm. With 0.01 ohm for the resistance, and 2 volts for polarization, it takes an electromotive force of 12 volts to send 1000 ampères through the bath, according to Ohm's law; this means that 85 per cent. of the power of the engines is wasted on sending the current through a diaphragm.

Moreover, the products formed are likewise conductors; the current will travel as well *via* the caustic soda, and another decomposition will set in, with evolution of oxygen. Hurter concludes that the separation of the products of the reaction from each other "offers almost insurmountable difficulties in the electrolytic process" [which, however, were soon completely overcome in practice!], and that "for the production of articles of low price electrolysis as a manufacturing operation is impracticable."

Hurter's observations are right in theory; but by arbitrary assumption of values they have led him to an entirely wrong con-



clusion, especially through the error that with porous diaphragms a difference of potential = 12 volts must be employed, and thus 85 per cent. of the mechanical energy must be wasted for overcoming the electric resistance and the polarization. We now know that with somewhat rational diaphragms the maximum voltage on the large scale is 4 volts for decomposing aqueous solutions of sodium chloride, when employing a proper current-density.

Since 1888, no doubt, Dr. Hurter has greatly changed his views; but a more recent communication of his (*Journ. Soc. Chem. Ind.* 1895, p. 428) does not contain much that is of practical utility, and his conclusions were strongly combated in the discussion of his paper.

A series of experiments on the chemical processes taking place in the electrolysis of aqueous solutions of chlorides has been made by Fogh ('Dissertation,' Dresden, 1889). Many of his results are deducible from the well-known properties of the galvanic current, such as these: that better results are obtained with hot than with cold solutions; better with concentrated than with dilute solutions; better with the electrodes near each other than at a greater distance. The secondary reactions were proved by obtaining much less chlorine than corresponds to the hydrogen, together with some oxygen, owing to the formation of hypochlorite, which gives off oxygen by the current. At a higher temperature the hypochlorite is changed into chlorate. When placing the anode below the cathode, so that the chlorine must pass through the caustic solution, no chlorine whatever escapes. When employing a diaphragm, first pure chlorine is given off, but gradually more and more oxygen gets mixed with it, by the diffusion of caustic liquor into the anode chamber, where hypochlorite is formed and is decomposed by the current into metal, oxygen, and chlorine. When working without a diaphragm in such manner that the chlorine at once acts upon the alkali and forms *hypochlorite*, this occurs only to a very limited extent; after a certain limit no more hypochlorite is formed and ultimately it even decreases, but irregularly, evidently not by an electrolytic decomposition, but by the action of the nascent hydrogen. But the whole of the KCl or NaCl can be gradually changed into *chlorate*, none of which is electrolytically decomposed so long as chloride remains present. Part of the chlorate is, however,

reduced by nascent hydrogen, which makes the industrial employment of electricity impossible except with very cheap power [this had been proved before Fogh by Gall and Montlaur, as we shall see].

Fogh distinguishes the following stages when electrolyzing a solution of NaCl at 10° to 15° C. without a diaphragm:—

A. *First Stage*.—(1) Electrolytical decomposition of NaCl into Na and Cl. (2) Decomposition of water by Na into NaOH and H. (3) Reaction of chlorine on NaOH; formation of hypochlorite.

B. *Principal Stage*.—(4) Simultaneous electrolytic decomposition of chloride and hypochlorite in the molecular ratio 15:1. Repetition of reactions 2 and 3. (5) Transformation of hypochlorite into chlorate and chloride.

C. *Secondary Process*.—Reduction of hypochlorite and chlorate by nascent hydrogen.

If the electrolysis is continued after the principal stage has been passed, the chlorate itself decomposes. In order to produce 2 mols. chlorate a quantity of current must be employed sufficient for disengaging 16 mols. of Cl from chloride. Since 2 chlorate correspond to 12 chloride, the principal process utilizes only  $\frac{12}{16} = 75$  per cent. of the current for the formation of chlorate. Of this, in the absence of a diaphragm, very much (in Fogh's case two-thirds) is decomposed by the nascent hydrogen, and thus only 25 per cent. of the current is utilized [Gall and Montlaur from the first worked *with* a diaphragm].

When electrolyzing calcium or magnesium chloride with a diaphragm, the insoluble hydroxide formed cannot return into the anode chamber; there are thus no secondary reactions, and almost the whole of the current is chemically efficient. This can be done with a voltage of 2·7 V, and thus by a horse-power (=630 watts) per hour 303 grms. Cl, 315·8 grms. Ca(OH)<sub>2</sub>, and 8·5 grms. H can be produced. Assuming the hydrogen to be utilized as fuel [which has not yet been realized anywhere], and putting a H.P.=627,840 calories, Fogh calculates 78,817 cal. for electrolytically generating 71 grms. chlorine and 74 grms. calcium hydrate, against 82,806 cal. for producing the same quantity of bleaching-powder from common salt, sulphuric acid, manganese, and limestone. [His calculation has no practical value.]

Nourrisson (Compt. rend. 1894, cxiii. p. 189) gives calculations and observations as to the minimum electromotive force required

for decomposing solutions of alkaline salts. His calculations are based on the principle developed on p. 636, dividing the difference in the heats of formation of the first and the second products by a constant (which he assumes = 23.2). In the case of NaCl he deducts from that difference (53 cal.) 6 cal. for secondary formation of chlorine and oxygen compounds, and thus obtains a minimum voltage of 2.02 V. [Oettel, in the paper quoted lower down, has shown that this deduction is not admissible, and that the minimum tension is really 2.30 V.] For decomposing  $\text{Na}_2\text{SO}_4$  Nourrisson calculates 2.15 V as minimum tension. For all oxysalts of the alkaline metals this tension is the same. His observations very nearly agree with his calculations; they showed the following minimum voltages:—

K,Cl	2.00 volts.	$\text{K}_2\text{SO}_4$	2.4 volts.	K, $\text{NO}_3$	2.32 volts.
Na,Cl	2.02 „	$\text{Na}_2\text{SO}_4$	2.4 „	Na, $\text{NO}_3$	2.36 „
Ca,Cl <sub>2</sub>	1.95 „	$(\text{NH}_4)_2\text{SO}_4$	2.29 „	Ca, $(\text{NO}_3)_2$	2.28 „
Ba,Cl <sub>2</sub>	1.94 „			Ba, $(\text{NO}_3)_2$	2.37 „
$\text{NH}_4\text{Cl}$	1.83 „				

[Oettel explains these low figures for the chlorides by errors of Nourrisson's instruments.]

Blanc (Compt. rend. cxviii. p. 411) has likewise made experiments on the minimum decomposing tensions, and he has found even slightly lower figures, viz., for K,Cl 1.96 volts; for Na,Cl 1.98 volts; for Ca,Cl<sub>2</sub> 1.89 volts; for  $\text{K}_2\text{SO}_4$  2.21 volts; for  $\text{Na}_2\text{SO}_4$  2.21 volts, &c.

Berthelot (*ibid.* p. 412) remarks that the results obtained by Nourrisson and Blanc can be deduced from a paper he published in 1882; calculation led him, *e. g.*, in the case of  $\text{KSO}_4$  to the formula  $\frac{15.7 + 34.5}{23.2} = 2.16$ , observation to 2.20 volts. In a further communication (Compt. rend. cxviii. p. 702) Le Blanc altogether doubts the applicability of thermochemical reasoning for the calculation of the galvanic polarization, to which Berthelot replies (*ibid.* p. 707) that the coincidence of the numerical results obtained by experience according to that method cannot possibly be explained by an accident. Nernst (in R. Meyer's 'Jahrbuch der Chemie,' iv. p. 64) emphatically confirms Berthelot's view, and adds that the modern theory of electrochemical processes is incomplete in this respect, since it is unable to explain the above-mentioned coincidence.

Oettel (Chem. Zeit. 1894, p. 69) corrects Nourrisson's figures (comp. above), and he adds some interesting observations of which we will give an abstract. If electrodes with rough surfaces are employed, the minimum of decomposing voltage can frequently be directly measured. On such rough electrode surfaces a sufficient quantity of liquid or gaseous products is condensed to convert the cell for a short time into a storage battery. After some time the current is shut off and an instrument with great resistance is put in, which allows of measuring the tension. Whilst a minimum polarization current is flowing through the measuring instrument, reactions occur inverse to those formerly taking place in the cell. The tension is observed just so long as both electrodes are still charged with the products of the reaction; when these have been consumed, the tension decreases. The time during which the polarization current shows the full decomposing tension depends on the size of the electrodes. In the case of common salt solutions, with electrodes of sheet-iron and retort-carbon and a porous clay diaphragm, Oettel observed with a Siemens tension galvanometer, with currents of from 3 to 60 ampères, a decomposing tension of 2.25 to 2.28 volts, or very nearly the calculated tension of 2.30.

In the clay diaphragm the solution of chlorine in salt solution, formed at the anode, and the solution of NaOH, formed at the cathode, meet and produce sodium hypochlorite. This in the cathode chamber is quickly reconverted into NaCl by the reducing action of the current; in the anode chamber it is partly oxidized into NaClO<sub>3</sub>, partly electrolytically decomposed in such manner that the Na migrates to the cathode and is there transformed into NaOH and O, whilst at the anode HOCl and O are found. In a similar way part of the chlorate is again electrolytically decomposed with formation of NaOH, H<sub>2</sub>, HClO<sub>3</sub>, and O; another part migrates into the cathode chamber and is there reduced to NaCl.

The formation of oxygen compounds of chlorine is therefore reducible to a purely chemical reaction between chlorine and caustic alkali, and their quantity is directly proportional to the velocity with which the two liquors diffuse through the diaphragm. Under equal conditions the velocity of diffusion increases with the difference of the solutions and the porosity of the membrane. This is in agreement with the fact that all the more hypochlorite is formed the more alkali is present in the cathode liquor and the

more porous the diaphragm. No certain observations are as yet available to prove a *direct* oxidation of the alkaline chloride to hypochlorite or chlorate by the electric current.

It is an established fact that in the electrolysis of the alkaline chlorides the chlorine evolved is mixed with oxygen, and this is usually ascribed to a secondary decomposition of the hypochlorite. The slight quantity of the latter which is formed is, however, insufficient to explain the frequently considerable quantities of oxygen. These can be traced to another process. The caustic alkali in the cathode chamber is likewise decomposed by the current into alkaline metal, hydrogen, and oxygen. The metal, of course, instantaneously regenerates the decomposed alkali, so that the result is that of decomposing water. The proportion in which the current, and with it the decomposition, divides itself between the caustic alkali and the chloride depends upon the concentration and alkalinity of the liquors. Two factors favour the passage of the current through the caustic alkali: the better conductivity of the latter in comparison with the chlorides and its smaller decomposing tension, which is equal to that of water, = 1.5 volts.

That part of the current which is absorbed by the decomposition of water is of course lost, and the current efficiency therefore decreases with the increase of the percentage of oxygen. The efficiency is even less favourable in the electrolysis of alkaline sulphates, for in this case *both* final products are good conductors, and the current simultaneously decomposes three substances—the original salt, the sulphuric acid, and the caustic alkali.

The above is in agreement with the fact that Fogh (p. 643) found the chlorine, separated from calcium or magnesium chlorides, free from oxygen and very pure. Here the hydroxides, separated at the cathode, take no part in conducting the current, and hence no oxygen is formed.

~ In opposition to the opinion held by many inventors, that in electrolyzing alkaline salt solutions sometimes *water* is primarily decomposed, Arrhenius (Zschr. f. phys. Ch. xi. p. 805) proves that this is not the case. Experiments showed that some time always elapses after closing the circuit before hydrogen is visible at a mercury electrode, whereas in sulphuric acid the hydrogen is immediately evolved; this undoubtedly proves the primary separation of alkaline metal and the formation of an amalgam.

The electromotive force required for electrolysis is influenced by the secondary reactions, and may sometimes be entirely dependent upon these. If the result of the secondary processes in various cases is the same as in electrolyzing alkaline salts, the electromotive force is the same and is independent of the nature of the salts. All known facts are in favour of the assumption that water alone, or in the presence of electrolytes, takes part only to an extremely slight extent in the conduction of the current and in the decomposition.

### *Costs of Electrolysis.*

Cross and Bevan, on the occasion of discussing some electrolytic processes (Journ. Soc. Chem. Ind. 1892, p. 963) give the following calculations, to which I add some remarks, enclosed in []. We have first to consider the cost of *power*. With large engines of the best kind, say two at 1200 H.P.=2400 H.P.,  $2\frac{1}{2}$  lbs. of coal per H.P. hour may be assumed. [This ought certainly to suffice.] We must then spend per 24 hours :—

	£	s.	d.
Coals $2400 \times 2\frac{1}{2} \times 24 = 64$ tons at 10s. ....	32	0	0
Labour, two shifts, eight men at 5s. ....	4	0	0
Depreciation 10 per cent. for 300 days :			
on engines   £10,000			
,, boilers     7,000			
	<hr/>		
£17,000 .....	5	14	0
Oil, waste, &c. ....	1	0	0
	<hr/>		
	£42	14	0

This divided by  $24 \times 2400$  comes to 0.18*d.* per H.P. hour; but to make sure, Cross and Bevan assume the cost of power=one farthing per H.P. hour. This agrees almost exactly with an estimate by Dr. John Hopkinson, according to which a Board of Trade unit (=1 kilowatt hour) can be produced at a cost of 0.33*d.* [Swinburne, in Journ. Soc. Chem. Ind. 1894, p. 455, states the cost of a kilowatt hour only=one farthing, inclusive of interest and depreciation.]

This 2400 H.P., when converted into electrical energy and delivered at the terminals of the electrolyzers, will be equivalent

to 2000 electrical H.P., on the basis of a loss in conversion and leakage of 17 per cent. This is  $2000 \times 746 = 1,492,000$  watts.

Very much depends upon the amount of the working voltage. With the Greenwood or Le Sueur process, Cross and Bevan assume working at a potential difference of  $4\frac{1}{2}$  volts [this is decidedly more than is required with other processes, and may therefore be accepted]. Dividing 1,492,000 watts by  $4\frac{1}{2}$  volts, we arrive at a current of 331,555 ampères = 7,957,320 ampère hours *per diem*.

Each ampère hour is theoretically capable of producing 0.00292 lbs. of chlorine, therefore  $7,957,320 \times 0.00292 = 23,235$  lbs. of chlorine per 24 hours. Taking a practical efficiency of 80 per cent. [which is a minimum], a current of 331,555 ampères will yield 18,588 lbs. of chlorine, equal to 22.43 tons of 37 per cent. bleaching-powder per 24 hours.

Each ampère hour will yield 0.0033 lb. NaOH. A similar calculation to the above gives us a yield of 9.378 tons of caustic or 12.426 tons of soda-ash per 24 hours.

The cost of these products is assumed by Cross and Bevan as follows:—

	£	s.	d.
18 tons salt at 12s. ....	10	16	0
12 „ lime at 12s. ....	7	4	0
Power $2400 \times 24 = 57600$ H.P. hours at $\frac{1}{4}d$ . ....	60	0	0
Labour .....	10	0	0
Casks and packages .....	18	0	0
Depreciation at 10 per cent. for 300 days : on electrolyzers..... £12,000			
„ dynamos ..... 8,000			
„ tanks, pumps, buildings, &c..... 10,000			
	<hr/>		
£30,000 ...	10	0	0
Superintendence .....	1	0	0
General expenses .....	4	0	0
	<hr/>		
	£121	0	0

For renewing the diaphragms and anodes in the Le Sueur process they allow £30; for producing carbonic acid in the same

process £2, thus making the cost of soda-ash=£153. In the case of caustic soda we must add the expense of evaporation, which they take at £1 per ton, that is £9. This caustic soda in many processes still contains some salt, which renders it rather less valuable than the ordinary product.

[This calculation applies on the whole to all electrolytic processes in which the voltage is not much more or less than  $4\frac{1}{2}$  volts, and is therefore of general interest. It must be acknowledged that most of the items are not estimated at all too low. The best triple-expansion engines certainly do not consume  $2\frac{1}{4}$  lbs. per H.P. hour;  $1\frac{1}{4}$  lbs. ought to suffice. Moreover, Cross and Bevan have increased the calculated figure from 0.18 to 0.25*d.*, that is by 40 per cent. With water-power much lower costs of power must be assumed. In Switzerland, *e.g.*, the cost of 1 *electrical* H.P. hour = 735 watts is reckoned = 1 centime, say  $\frac{1}{10}$ *d.* At the Niagara Falls they reckon 18 per electrical H.P. per year, which is about equal to  $\frac{1}{8}$ *d.* per H.P. hour for 300 working days. The potential difference of  $4\frac{1}{2}$  volts also exceeds what is necessary; theoretically only 2 volts is required for the electrolysis itself (p. 645), and  $2\frac{1}{2}$  volts for resistance and polarization is decidedly more than necessary, at least by  $\frac{1}{2}$  volt. Cross and Bevan state their figures to represent maximum costs. The wear and tear of the anodes, if they are properly chosen and joined with the conductors in a suitable manner, not acted upon by chlorine, must be much less than they assume. It is certainly very doubtful whether Greenwood's diaphragms will, as the inventor states, last for ever. The necessity of frequently renewing the diaphragms in Le Sueur's and similar processes is certainly a weak point, and £30 may *not* suffice in this case. Indeed, nearly everything depends upon employing good anodes and diaphragms. That process is also very irrational in converting the soda into bicarbonate and reconverting this into soda-ash, the cost of which operations is decidedly *much* more than £2 for 12 tons. On the other hand, the conversion of a 10 per cent. caustic-soda solution, containing a very large quantity of common salt and a little sodium chlorate &c., into solid caustic soda is much more troublesome and expensive than is generally assumed. There is also nothing allowed for heating the baths. Still, on the *whole*, the above calculation is probably much too high, and with a *good* process the costs should be less.]



The *value of the products obtained* is stated by Cross and Bevan as follows:—

	£	s.	d.
22·43 tons bleaching-powder at £7 10s.	168	4	6
9·878 „ caustic soda at £12 10s.....	112	10	9
	<u>£280</u>	<u>15</u>	<u>3</u>

or else:

22·43 tons bleaching-powder, at £7 10s.	168	4	6
12·426 „ soda-ash, at £5 15s. ....	71	9	0
	<u>£239</u>	<u>13</u>	<u>6</u>

[This calculation is based on the prices then current, which are now very different; it is, however, given in order to show how irrational are those processes in which the soda is not obtained as caustic, but as carbonate.]

A further calculation of the cost of an electrolytic soda and chlorine works is given by Häussermann (*Zsch. f. Electrochemie*, 1895, p. 21). He starts with a daily production of 5000 kil. NaOH, and the corresponding quantity of bleaching-powder from brine; steam is assumed to furnish the power, with continuous working over 350 days per annum. [N.B. 300 days is enough.]\*

1. *Power*.—1 ampère furnishes, with 80 per cent. efficiency, in 24 hours 28·56 grams NaOH and 25·2 grams Cl; hence 1 kil. NaOH per 24 hours requires 25 ampères. The baths require a voltage of 3·5 volts [N.B. it is better to allow 4 volts], or for 1 kil. NaOH 122·5 watts, for 5000 kil. 612·5 kilowatts=832 elect. H.P. At the same time we obtain 4410 kils. Cl, which is practically equal to 12,500 kils. 35 per cent. bleaching-powder [N.B.]. The 832 electrical H.P. is=915 indicated H.P.; adding 85 H.P. for other purposes, we arrive at 1000 H.P. The best engines consume 0·8 kil. [=1½ lbs.] coal per H.P. hour, or altogether 19,200 kil.; at 1·2 mark=220·4 marks†. For firemen, enginemen, oil, repairs, depreciation, &c., according to experience, about the same amount as the above should be assumed; total cost, therefore, 460·8 marks (say £23).

\* I mark with N.B. the assumptions which seem to me too favourable.

† Where coal is so dear, viz. 12s. per ton, electrolysis is scarcely practicable.

2. *Salt*.—Allowing a loss of 10 per cent., we require 8000 kils. rock-salt, at 1·5 mark=120 marks. Saturated brine is cheaper. [N.B. Certainly! The above price=15s. per ton of salt would be prohibitory.]

3. *Evaporation of the liquor and finishing the caustic*.—The liquor, as it comes from the baths, contains 80 grams NaOH per litre, apart from the NaCl; hence per 24 tons 63 cub. metres must be worked up. This must first be boiled down to spec. grav. 1·45, in which operation the common salt, which is but slightly soluble even in hot concentrate caustic liquor, precipitates almost completely. For this purpose multiple-effect apparatus should be employed (comp. Vol. II. p. 765), preferably those provided with an automatic arrangement for taking away the salt, like those of Neumann and Esser, Germ. pat. 75421. In this way 1 kil. of coals will evaporate 20 kils. water, and as we have to remove 50 cub. metres of water, we require  $2\frac{1}{2}$  tons of coal =30 marks. For finishing the caustic we may allow another 5 tons=60 marks.

4. *Quicklime* for bleaching-powder, at 60 parts for 100 parts bleach=7500 kils., costing 15 m. per ton=112·50 marks.

5. *Packages*.—5 tons of caustic require iron drums at 12 marks per ton=60 marks,  $12\frac{1}{2}$  tons bleaching-powder casks at 17 m. per ton=212·50 marks.

6. *Wages*.—Häussermann gives details for estimating these at 182·50 marks.

7. *Repairs*, inclusive of renewing anodes and diaphragms, arbitrarily assumed at 175 marks.

8. *Depreciation*.—He allows 360,000 marks for buildings and 40,000 for a well, chimney, and fence, all at 5 per cent., or 57·15 marks per day. The depreciation of the boilers and engines is included in the costs of power. The other apparatus—baths, vacuum pans, finishing-pots, bleaching-powder chambers, workshops—may be assumed=600,000 marks, at 10 per cent. depreciation 171·42 marks per day, or altogether 228·57 marks.

Summary of costs of 5000 kils. caustic soda and 12,500 kils. bleaching-powder:—

	Marks.
1. Power .....	460·80
2. Salt .....	120
3. Coals .....	90
4. Lime .....	112·50
5. Packages .....	212·50
6. Wages .....	182·50
7. Repairs .....	175·00
8. Depreciation .....	228·58

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1581·88, say £79.

To this must be added general expenses (salaries, office expenses, brokerage, insurance, sick fund, rates, and taxes), amounting to 25 per cent. of the other costs or upwards.

[This would amount to about £100, and would leave a handsome profit at the market prices in 1895. But these prices, especially that of bleaching-powder, will in all probability be considerably reduced, as soon as the "combinations" fail, which is inevitable in the end. On the other hand, some of Häussermann's assumptions, as denoted by the sign "N.B.," are much too high. Large electrolytic works must be established under very much more favourable conditions as to cost of power and salt than he has assumed.]

## CHAPTER XXV.

SPECIAL PROCESSES FOR THE ELECTROLYTIC PRODUCTION  
OF SODA AND CHLORINE.I. PROCESSES FOR THE PRODUCTION OF ALKALI AND CHLORINE  
WITHOUT PREVIOUS SEPARATION OF ALKALINE METALS.

THE first who is generally credited with an attempt at utilizing electrolysis for the alkali manufacture is William Cooke, whose English patent, No. 13620, dates May 3, 1851. It has, however, been overlooked that this patent was taken as a "communication;" the real inventor, unknown by name, was probably a foreigner.

Cooke describes the following "improvements in the manufacture of soda and the carbonate thereof." A large tank, 11 by 6 by 3 feet, is divided into three compartments by means of porous diaphragms. Two copper plates are placed in the middle compartment and large pieces of iron, all connected together, in each of two other compartments. Each copper plate is connected by a slip of copper with the next mass of iron. A solution of common salt is put into each compartment with the iron, and clean water in the compartment with the copper. The vessel is covered up, "and the temperature being now kept above 70° F., the decomposition of the salt will be accomplished within seven days." The soda in the middle compartment is in solution "with a little salt," and the liquid may be evaporated from it. "The caustic soda when dry must be kept hot and stirred for an hour or two, during which time it will absorb the carbonic acid from the air with great avidity; it will greatly increase in bulk, and will be finally converted into pure carbonate."

The last remark shows that the inventor had, at the best, made a laboratory experiment on a minute scale, perhaps not so much as that. This is still further proved by his assertion that with the above crude kind of battery a ton of carbonate of soda could be made within seven days, and that this required 2489 lbs. common

salt and 1161 lbs. iron (which is converted into chloride in the outer compartments). These figures are almost exactly the chemical equivalents, and are evidently only calculated on paper.

Soon after (pat. No. 13755, Sept. 25, 1851) Charles Watt, together with many other things, describes the electrolysis of common salt. He goes a step beyond Cooke, by not combining the source of electricity with the decomposing cell, but creating it outside by means of a Daniell's battery of six cells. The decomposing vessel is divided by porous partitions into two or more compartments, all of them filled with a strong solution of salt and containing the electrodes; movable covers serve for collecting and conveying away the gases which are generated. One of these is chlorine; the hydrogen is to be used for heating purposes. The working temperature should not be below  $49^{\circ}$  C. In this process caustic alkali is obtained; if carbonate is to be produced,  $\text{CO}_2$  must be employed. If hypochlorites or chlorates are to be produced, steam-jacketed vessels are employed, containing two electrodes, one above the other, the lower for the liberation of chlorine, the upper for that of alkali. A hot solution of the chlorides, to which a certain quantity of free alkali or alkaline earth has been added, is put into the vessel, and connection is made with the battery. If it is desired to produce a hypochlorite, the temperature is kept between  $37^{\circ}$  and  $49^{\circ}$ ; the solution may be used as a bleaching-bath. If a chlorate is to be produced, the temperature is raised. The evolved hydrogen is specially collected.

Stanley once more takes a patent, No. 811, 1853, very similar to Cooke's; here also the iron is to be converted into chloride.

Dickson (Nos. 2044 and 2265, 1862) patents, in a most confused manner, the decomposition of common salt, kelp, crude nitrate of soda, soda with ammonium chloride from the ammonia-soda process, Leblanc black-ash, &c., in heated cast-iron cells with carbon anodes. His second patent refers to the electrolysis of sodium chloride, this time with the addition that the decomposition was to be assisted by nitric, nitrous, sulphurous, or sulphuric acid, ferrous or ferric chloride, cuprous or cupric chloride, ferric or cupric oxide, or by passing oxygen obtained by electrolysis through certain ignited chlorides, or by the galvanic decomposition of fused common salt. This medley requires no criticism.

Fitzgerald and Molloy (No. 1376, 1872) again patent the electrolysis of sodium and potassium chlorides, alkaline nitrates

and sulphates, calcium chloride or hydrochloric acid, for the production of free chlorine, of hypochlorites, chlorates, &c. They make a large number of statements as to the baths, diaphragms, and anodes to be employed.

A statement made in the 'Berichte der deutschen chemischen Gesellschaft' (vi. p. 1141), according to which the above process was being applied at sea-side places, *e. g.*, St. Lawrence, near Margate, on a large scale, and successfully, for the electrolysis of sea-water (!), was, of course, entirely devoid of foundation.

Faure (No. 1742, 1872) returns to Cooke's principle, but employs a thermoelectric current. He uses cast-iron anodes with carbon steps, and a porous diaphragm made of canvas. In the negative cell ferric oxide may be placed. The products are caustic soda and ferric chloride, whose solutions run away by separate channels.

Lontin (No. 473, 1875) patents the employment of dynamos for the decomposition of alkaline chlorides, together with a large number of other electrolyses. (Since the title of the patent mentions only acetic and formic acid, it would have been invalid in all other cases.)

Wastshuk and Glukoff (Engl. pat. no. 4985, 1880) employ for the electrolysis of common salt a closed elliptical trough with porous diaphragm. On the right side is the anode, consisting of carbon or platinum, on the left the iron cathode; both compartments are filled with brine. The current liberates chlorine on the right side; this partially acts upon water, so that HCl and O are formed. The gases are freed from HCl by washing; Cl and O are given off and are utilized for a gas-battery. On the left side Na is formed, which instantly decomposes with water into NaOH and H; the hydrogen equally goes into the gas-battery. The brine is supplied from a higher reservoir equally to both compartments; the pressure produced thereby causes a quicker removal of the gases and lessens polarization. The feeding with brine and the running off of the caustic-soda solution are regulated in such manner that the latter gives only a slight opalescence with silver nitrate [such complete decomposition is practically impossible!]. From the caustic-soda solution either solid caustic soda or, by carbonizing, sodium carbonate is to be obtained. The current produced by the gas-battery is to electrolyze brine in a second bath.

L. Wollheim (Germ. pat. 16126, of 1881) employs different liquids in the two chambers of the decomposing cell divided by the diaphragm. In the cathode cell he places caustic soda or potash, in the anode cell sodium chloride, carnallite, &c. The caustic-soda solution, which is always getting stronger, is continuously removed from the bottom of the anode cell, and the solution of the chloride is supplied continuously to the top of the cathode cell.

Spence and Watt (Engl. pat. 1630, 1882) employ in both chambers, divided by a plaster-of-Paris diaphragm, electrodes made of retort-carbon. The hydrogen given off at the cathode is to be employed for driving a gas-engine by which the dynamo is driven, and they believe this to be economical work. Of course they cannot have assumed that they would save in this way the whole of the power for the dynamo, since that would be a *perpetuum mobile*.

Geisenberger (Engl. pat. 3104, 1883) electrolyzes a solution of zinc chloride.

Richardson and Grey (Engl. pat. 4417, 1884) once more very naively patent the electrolysis of common salt, as if nobody had the idea before them, and without describing a technically available apparatus for the purpose.

Höpfner (Engl. pat. 6736, 1884) specially occupies himself with the loss produced by polarization. To prevent this, he employs at the cathode depolarizing substances, or a continuous circulation of the liquid. As anode he employs a substance not acted upon by chlorine, as carbon or manganese ore; the solution of the chloride is constantly run in and out, so that the chlorine produced is carried away. According to the rate of the feed, the liquor is more or less saturated with chlorine. In order to prevent the evolution of hydrogen at the cathode, this, which may consist of any good conductor, is coated with some substance reducible by hydrogen, and thus preventing polarization. (His process was specially intended for producing a solution of chlorine in brine, for the purpose of extracting gold.)

In a further patent (Germ. pat. 80735) Höpfner employs a solution of cupric chloride as a depolarizer in the cathode chamber. The  $\text{CuCl}_2$  is reduced by the current to  $\text{CuCl}$ , which is kept in solution by the  $\text{NaCl}$  or  $\text{HCl}$ ; later on it is again oxidized to  $\text{CuCl}_2$  by air in acid solution, and thus reintroduced into the

process. This permits of generating far more chlorine than would be the case with the same amount of current.

Phillips (1885) places a porous earthenware cell in a wooden trough, 4 inches from the bottom. The cell is closed by a cover with three perforations. Through one of these a glass tube, communicating with a compressed-air main, passes through to the bottom of the cell; the second contains a gas-delivery pipe; the third the carbon anode. The cathode consists of platinized copper. The trough and the earthenware cell are half-filled with brine, and the current from a gramme machine is passed through it, the chlorine formed being quickly removed from the cell by the compressed air. Phillips admits that the brine cannot be completely converted into caustic liquor by this means.

Tricket and Noad (Engl. pat. 7754, 1888), in electrolyzing NaCl, again apply the chlorine for combining with a metal present at the anode. This is employed as an oxide, and is regenerated from the chloride by roasting. The clear caustic liquor is to be treated with calcium carbonate, which yields its  $\text{CO}_2$  to it, and at the same time precipitates any traces of metals &c. Herein consists the only novelty in this patent.

Greenwood (Engl. pat. 14239, 1888) employs a large trough, containing a number of carbon electrodes, in an annular group, communicating with the negative pole of a dynamo. In the centre is a porous cell, also containing carbon as an anode. The outer vessel is fed with concentrated brine, the inner with water; the outer vessel yields caustic liquor, the inner a solution of chlorine in water.

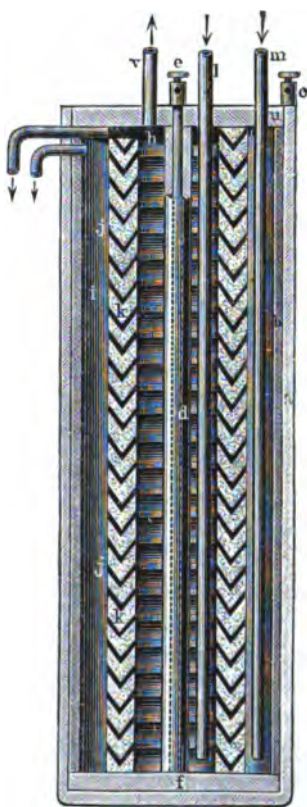
Further patents of the same inventor (Nos. 18990, 1890; 2134, 1891) describe the following apparatus:—The bath consists of iron or of carbon, externally coated with electrolytically precipitated copper; this is the cathode. The anode is formed by a metal cylinder coated with carbon. At a suitable distance from both is a diaphragm, consisting of a number of V-shaped porcelain or glass troughs, placed one inside the other. The interstices are filled up with asbestos or ground steatite. This diaphragm is said to offer very little electrical resistance and to prevent the diffusion of chlorine from the anode chamber into the caustic liquor present in the cathode chamber. A number of such baths are put in series; the brine flows from a higher reservoir through all the baths, then into special vessels, from which it



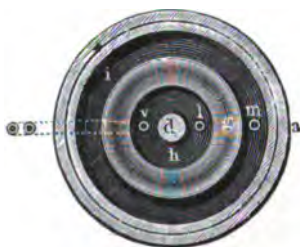
returns into the reservoir, and so forth, until it is sufficiently decomposed. The baths are provided with porcelain covers, through which passes the chlorine pipes. In another arrangement the bath is of an oblong shape, and is divided into anode and cathode chambers by parallel plates, forming the poles and diaphragms; in this case the cathodes are not coated with carbon. The liquor formed by the electrolysis contains, together with NaOH, much undecomposed NaCl, which must be removed by evaporation and fishing out.

Figs. 192 and 193 show a longitudinal and cross-section of one of the decomposing cells, which are placed terrace-wise (a perspective view of the apparatus is given in 'Industries,' xii. p. 210). *a* is the outer wall of the cathode chamber; *b* its carbon lining (which is not required in the case of iron); *c* the negative-pole connection; *d* the anode cylinder of carbon-coated metal, with the positive-pole connection *e*. The anodes are made by electrolytically coating with copper the two faces of the carbon slabs to be joined together, then tinning them, placing the slabs in a mould with those two faces turned towards each other, but leaving an empty space between them which is filled by pouring in melted type-metal. The carbon is made non-porous by rubbing it with lead peroxide and polishing. Anode *d* is insulated from cathode *a* by a slate slab *f*. Between *d* and *a* is the diaphragm *g*, formed by the V-shaped porcelain troughs *j* with

**Fig. 192.**



**Fig. 193.**



the asbestos or steatite filling *k*. This forms an anode chamber *h* and a cathode chamber *i*, which are filled from below with brine by pipes *l* and *m*; *u* is a porcelain cover, *v* the outlet-pipe for chlorine.

On the large scale the above-mentioned arrangement seems to have been employed, in which oblong vessels are divided by the described diaphragms into ten anode and ten cathode chambers; the cathodes are cast-iron plates. The anodes and cathodes of each bath are parallel, and five such groups of baths are put in a stepped series. With a current density of from 100 to 110 ampères per square metre the tension is 4.4 volts. The brine flows from the top vessel downwards to the bottom one; it is again raised by an ebonite pump, and this is repeated until the maximum of useful electrolysis is attained, which, according to Greenwood, is the case when the liquor contains 2.21 per cent. NaOH to 10.76 per cent. undecomposed chlorine. The expert Preece calculates the cost of decomposing a ton of salt at £3 8s., allowing one farthing as the cost of a kilowatt hour, which infers cheap coal and triple-expansion engines.

Nahnsen (Engl. pat. No. 11699, 1890) prescribes electrolyzing at between 0° and 7°, in order to prevent the reaction of chlorine on the water. Insoluble electrodes must be employed, carbon as anode. The voltage is to be 20 to 30 per cent. above the theoretical, the current-density at the anode not below 0.25 ampère per square decimetre.

Richardson and Holland (No. 2296, 1890) try to prevent the agitation of the liquid and the polarization of the cathode by the hydrogen given off there, by coating the cathode with cupric oxide, which is thus reduced to copper and easily transformed again into CuO. For the manufacture of caustic alkali the electrodes are placed horizontally, the cathode at the bottom, the anode at the top. The heavy caustic soda remains at bottom, the chlorine escapes at the top. If hypochlorites are to be manufactured, the electrodes are placed in the opposite order; the chlorine on rising then meets with the caustic soda and combines with it. For small-scale work vertical electrodes with porous diaphragms, and a zinc anode instead of carbon, may be employed; the whole will thus act as a galvanic battery, and may be utilized as such.

In a subsequent patent (No. 19704, 1891) Richardson prescribes constructing the cathode as a broad band moving through the cell; on its entering into the electrolyte the cupric oxide is put

on, and on its leaving the reduced copper is removed. Instead of making the cathode itself movable, the depolarizator may be moved along it.

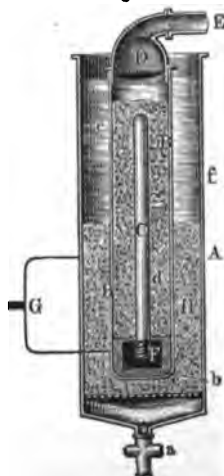
Another patent by Holland and Richardson (No. 2297, 1890) replaces the expensive and fragile porous diaphragms, which offer great electrical resistance, by non-porous partitions, which catch up the substances formed in electrolysis and carry them to the surface, the hydrogen taking along the caustic soda. In one of their apparatus, for instance, each electrode is covered with a kind of funnel; from the point of one the chlorine, from that of the other hydrogen and caustic soda are drawn off.

A further patent of Holland's (No. 5525, 1893) contains nothing of much importance.

Holland and Richardson's patents were carried out on a large scale at the Snodland paper-mills in Kent, and in getting up a Limited Company for the purpose of developing that process some remarkable statements were made concerning the results obtained at Snodland. Thus a Mr. Leith states, as one of the advantages of the process, that most manufacturers have an excess of steam-power, which they might utilize for driving a dynamo! From the report of a more competent expert, an electrician, we learn that at first, with iron cathodes, the high tension of 6 volts was required, which ought to have deterred any experienced person from employing such a process. Nine months later, when employing the patent copper cathodes, the tension had decreased to 3·8 volts—that is, about the same as is attained in any reasonable process with an ordinary iron cathode! The anodes made of retort-carbon are praised as a special advantage by the experts, as if they were peculiar to that process! The calculations of cost show an immense profit, *on paper*. In 1894 a factory was to be erected at St. Helens for decomposing 50 or 60 tons of salt by this process.

Cutten (Engl. pat. No. 88, 1892) tries to prevent the reunion of soda and chlorine by drawing off the chlorine at the top, while the caustic-soda solution sinks to the bottom by its own specific gravity (?). Brine

Fig. 194.



is continuously introduced below the anode and carried away above. His apparatus is shown in fig. 194.

The iron tank A forms the cathode, with the conductor G. The anode C is contained in a block of retort-carbon F, coated with insulating material *b* and placed at the bottom of the earthenware diaphragm B. This is porous only in its central portion *d*; above and below, at *c* and *e*, it is glazed and non-porous. Between B and the bottom of A space is left for collecting caustic-soda liquor, without touching the diaphragm. The upper part of the inside of A is coated with varnish or another insulator *f*; this is to confine the formation of NaOH to the cathode-surface below *f*, and to keep the solution of NaCl at the top as free from NaOH as possible. Tap *a* serves for drawing off the caustic liquor from C; cover D and pipe E are connected with the chlorine-pump.

Le Sueur (Engl. pat. 5983, 1891) describes the following apparatus:—A large tank is half-filled with the solution to be electrolyzed. One, two, or more cylindrical bells are placed therein, bottom upwards, in a rather slanting position, so that one edge is a little higher than the other. The upper part of the bells contains a large anode, made of gas-carbon, which is easily raised or lowered. The mouth of the bell is covered with a diaphragm made of parchment-paper or the like, and just below is the cathode made of wire gauze. The caustic soda is formed in the large tanks; the hydrogen easily escapes from the lower side of the bell, owing to its inclination, and chlorine is obtained from its top. The specification contains detailed descriptions and drawings for the lutes, for the electric connexions which permit of treating each bell independently of the others, for the attachment of the diaphragms, the carrying away of the gases, and so on.

A further patent (No. 15050, 1891) prescribes reducing the drawback of diffusion or leakage from the anodes into the cathode chamber by keeping the solution within the anode chamber constantly at the same composition, for which object hydrochloric acid is added to neutralize any NaOH carried in by diffusion.

Le Sueur's process is described by Cross and Bevan (Journ. Soc. Chem. Ind. 1892, p. 963). The electrolyzers consist of an iron tank with a sloping floor, on which rests the cathode. This is formed of a ring of iron filled with several pieces of iron-wire gauze. Several small holes are drilled in the top part of the ring to allow of the easy escape of the hydrogen. The floor of the

tank is also sloped for this purpose. The diaphragm rests on the cathode. It consists of two parts, viz., a sheet of ordinary parchment-paper and a double sheet of asbestos, cemented together by means of coagulated blood-albumen. The diaphragm being placed in position, the inner vessel of earthenware is placed on it, and by its own weight makes a water-tight joint. There are usually 6 to 12 electrolyzers in each tank. Inside the vessel has been previously placed the anode. This consists of pieces of ordinary retort-carbon imbedded in a mass of lead, through which electrical contact is obtained. By means of porcelain lutes any one electrolyzer can be electrically disconnected from the others in the same tank. The cell being in position, a saturated solution of salt is run into the outer vessel until it reaches just above the upper edge [of the inner vessel?]. The anode section is filled with similar solution to a level about half an inch above that of the solution in the cathode section. The object of this is to prevent any transference of solution from the outer to the inner vessel, this being more harmful than the reverse. The diaphragms are renewed every 48 hours; to effect this the whole of the inner vessels in any tank are simultaneously raised. [This frequent removal of the diaphragms is a serious objection to Le Sueur's process.] As the carbon of the anodes wears away, they are lowered by screws, so as to bring them as near as possible to the cathodes. After working from 6 to 8 weeks the anodes have to be renewed. For this purpose the cells are taken to pieces, and the lead is melted and recast. When the electrolysis has been continued long enough for the solution of caustic to reach a strength of about 10 per cent., the liquor is run away and the alkali precipitated as bicarbonate. [This part of the process is also very faulty in an economical sense!]

Cross and Bevan also discuss the cost of the process. We have referred to this in another place (p. 648); here we have only to mention that, according to their statement, the process was at that time (November, 1892) in operation at Rumford Falls, U.S.A., on a scale of 3 tons bleaching-powder *per diem*, and that a small experimental factory was in operation in London. Later on (Journ. Soc. Chem. Ind. 1894, p. 453) Cross stated that the Le Sueur process had been in regular work for two years, that it yielded an efficiency of 85 per cent., and that the difficulties connected with the anodes and diaphragms had been nearly surmounted. [For all

that the necessity of constantly changing the diaphragms, and the conversion of caustic soda into bicarbonate, must be considered very weak points of this process.]

Rieckmann (Germ. pat. 60755) describes various improvements in electrodes and other parts of the apparatus (figs. 195 and 196). The anodes consist of retort-carbon, of which a number of pieces  $b_1$

Fig. 195.

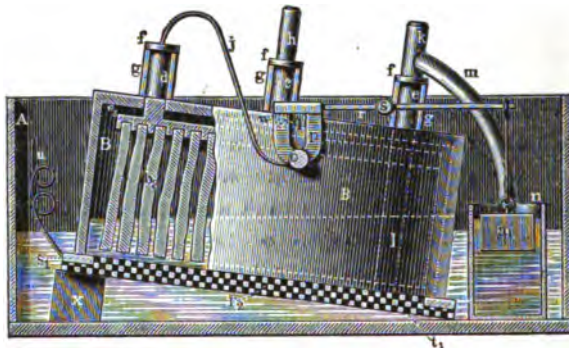
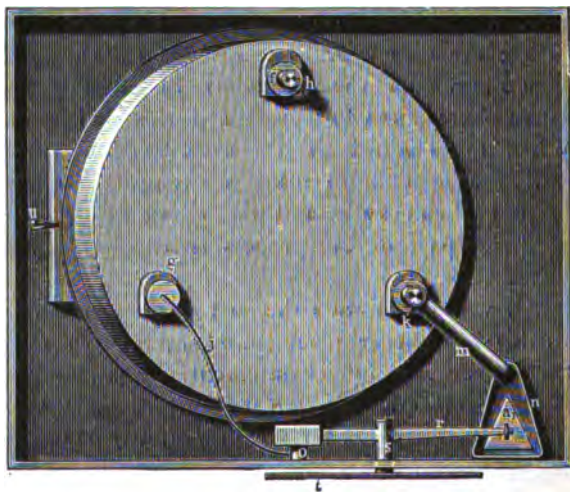


Fig. 196.



(fig. 195) of the same length are fixed in a lead plate  $e_1$ , suspended in an earthenware bell B, which is drawn over three tubes  $c, d, e$ , fixed to the lead plate  $e_1$  and made of lead pipe. Exchangeable pieces  $g$

are placed between the top of the bell and enlargements *f* fixed to the tubes. When the electrodes are worn out, the pieces *g* are replaced by others, by which the electrode is lowered down within the bell. The tube *c* serves at the same time for carrying away the chlorine through pipe *h*. In *d* the positive conductor *j* is fixed by lead being cast round it; *e* serves for the passage of one of the limbs of a siphon. These tubes are cemented into the openings of the bell with asphalt and asbestos, or the like. The cathode *t*<sub>1</sub> consists of several layers of wire gauze, set in the ring *s*<sub>1</sub>, connected with the negative conductor *u*. The cathode *t*<sub>1</sub> is in a sloping position, one side resting on the bottom of the tank, the other one on block *x*. On the ring *s*<sub>1</sub> a diaphragm *r*<sub>2</sub> is placed, made of asbestos or parchment-paper, and then the bell B is put on. The edge of the bell fits as tightly as possible on *s*<sub>1</sub>; the hydrogen bubbles also act in making the joint good by pressing the diaphragm against the edge of the bell. The diaphragm is placed at a short distance from the anode, which causes it to be less acted upon by the chlorine. The bell is, by means of the siphon, filled with so much solution of salt that the liquid within is a little above the level of the liquid in tank A; this pressure prevents the diaphragm from being forced inwards by the pressure of the hydrogen bubbles; it also serves for an automatic interruption of the current. The glass limb *l* of a siphon passes through tube *e* to a little below the anode; the outer (leaden) limb *m* dips into the vessel *n*, which is filled with brine up to the level of the liquid within the bell. The weight *a* dips into *n*; it is suspended from lever *r*, which is connected with a support *t* (fig. 196) by means of the pivot *s*, and forms the anchor of a horseshoe-magnet *p*, with whose metal support *o* the conductor *j* is connected. One of the limbs of the magnet *p* contains a depression *q*, filled with mercury, into which dips a pin *w*, fixed to the anchor part of lever *r*; the latter is electrically connected with the respective pole by the pin *s*. So long as the level of the liquid in *n* is not essentially changed the weight does not act and the circuit is closed; but if the liquid in the bell decreases, *e. g.*, by the joint of the diaphragm becoming leaky or the diaphragm being torn, the siphon begins to act; it draws liquid from *n* into the bell, and the weight now pulls at lever *r* all the stronger the more it becomes exposed; at last it pulls the anchor off and lifts the pin *w* out of the mercury, so that the circuit is interrupted. In order to pre-

vent the chlorine from collecting in the lever *l*, *m*, this is prolonged at the junction of both limbs into a leaden branch-pipe *k*, which communicates with a gas-pipe.

Kellner (Engl. pat. 5547, 1891) describes an apparatus similar to a filter-press, consisting of a number of frames divided by porous diaphragms. The successive frames form alternately anode and cathode chambers, with outlets for the liquid in opposite directions. They are all fed by a common channel in the bottom, down to which the diaphragms do not extend. The electrodes are carbon rods, mounted and electrically connected so that they can be singly removed without interrupting the work. By one of the side channels caustic-soda solution, by the other chlorine and chlorinated liquor are constantly removed.

A similar filter-press like apparatus is described by Guthrie (Engl. pat. 24276, 1893).

Kellner (No. 9346, 1892) further describes an iron cathode trough, with partitions cast on one side, not reaching quite to the other side. In the intermediate spaces are glass or earthenware frames, containing the anodes and diaphragms. The whole space between the diaphragms is filled with ground coal, in which carbon rods or plates are placed as anodes. The diaphragms consist of perforated slate or glass, so arranged that the holes in one diaphragm correspond to solid places in the next.

Blackman (Engl. pat. 19170, 1892) utilizes the difference of density between the electrolyte and the product of electrolysis for separating them. The electrolysis takes place in a quickly revolving vessel, in the central part of which an outlet for chlorine and another for hydrogen are fixed. The caustic soda separates at the cathode from the brine (?), forms an annular layer on the outside, and by a small opening drops into a tank. The iron vessels serve as cathodes; the anodes are made of carbon.

Craney (Engl. pat. 16822, 1892; 9295 and 9297, 1893) employs a wooden tank with a tightly fitting cover, the bottom of which is entirely covered with an indestructible porous substance, as ground slate or glass. Partitions, serving as cathodes, divide it into compartments in such manner that the liquid must always run above one and below the next compartment. The anodes consist of carbon, and are enclosed in non-porous stoneware bells, open below and projecting into the porous substance; they rest on the bottom of the tanks with their nicked-out edges. The anodes



may also consist of open porcelain, stoneware, or glass tubes, filled with compressed powdered carbon. The electrolyte circulates through the porous material on the bottom of the tank.

The best form of Craney's apparatus is shown in fig. 197. The anode chamber B consists of conical parts with outer ribs, so that on their being placed one into another projections *a* are formed. The upper part C projects above the liquid. Chamber B may also be made of a single pipe, with openings slanting in an upward and outward direction. Other forms of his electrical cells are shown in patents Nos. 11105, 11106, 11107, 11108, 17127, all of 1893; also 6126, 9761, 9949, of 1894.

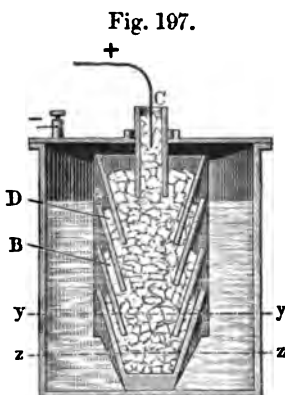
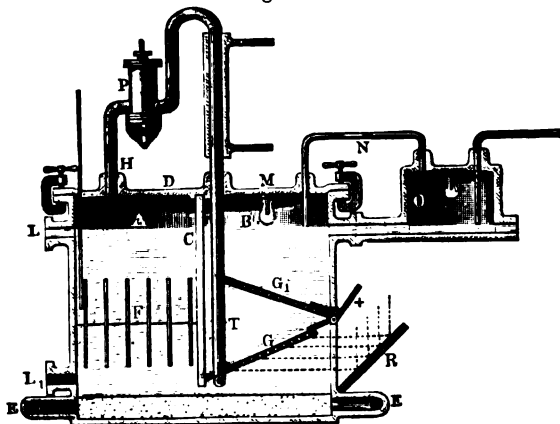


Fig. 197.

Roubertie, Lapeyre, and Grenier (Eng. pat. 15113, 1892) prepare NaOH and *hydrochloric acid* as follows:—A tank, lined with glass, is divided by a partition C, fig. 198, into two chambers A and B, filled to the lower edge of C with powdered salt; two pipes E

Fig. 198.



supply both chambers from below with saturated brine. A contains the negative electrodes F, consisting of upright, square, connected plates. B contains the sloping positive electrodes G G', consisting of silvered metal, lead, silvered glass, or carbon. A is

closed air-tight at the top; the hydrogen is drawn away from H by pump P and forced into the positive chamber B, where the pipe T is continued into a perforated cross-pipe, from which the hydrogen bubbles rise, following the slanting electrodes G G<sub>1</sub>, and combine with the Cl<sub>2</sub> liberated here, to form HCl, which flows away laterally by O. At the negative pole the soda formed is carried upwards by the hydrogen and flows away laterally at L; chamber A can be emptied by L<sub>1</sub>. Or else brine is run in at the top and the caustic liquor is drawn off at the bottom. The specification describes some other apparatus for the same object.

Andreoli (Germ. pat. 75033) describes an apparatus consisting of a shallow basin with cross chambers at both ends and parallel rows of anode and cathode cells in the centre, which are divided into two superposed chambers, in such manner that each left-sided top chamber is electrically equivalent to each right-sided bottom chamber, and *vice versa*. The liquor is made to circulate systematically by a pump; chlorine and hydrogen are drawn off as they are liberated. The caustic liquor is saturated with salt only so far as needful; the chlorinated liquor, however, is kept at unchanged density by a constant supply of salt. The work goes on in continual rotation, and the yield of Cl<sub>2</sub> and NaOH is stated to be nearly quantitative.

Faure's apparatus (Engl. pat. 16262, 1892) consists of porous brick walls with non-porous tops. The diaphragms, likewise made of porous bricks, run parallel with those walls. Each two elements are separated by a partition of loam, carbon, bitumen, and pebbles, converted by strong heating in a furnace into a non-porous conducting electrode. These elements stand on a water-tight insulating foundation of flags, coated with bituminous loam. On both sides of the electrodes coke is piled up, which protects them against the destructive action of chlorine and caustic soda, but which gradually consume it. The cathodes may also be protected by cast-iron plates cemented upon them. In order not to obtain too much HOCl together with chlorine at the anode, first a solution of sodium sulphate or sulphuric acid is introduced, and to this solution during the electrolysis an alkaline chloride is gradually added. The sulphuric acid becomes concentrated in the anode chambers filled with coke, forms HCl with the NaCl, and this drives out all chlorine from the hypochlorite. The solution of salt, before entering, is heated to 20° or 30°, and in the bath itself is further heated by the electrolysis to 60°, which produces

the evolution of the chlorine and increases the conductivity of the liquid. The gases consist of chlorine, oxygen, and  $\text{CO}_2$  (from the coke). They are passed through red-hot coke, in order to convert the  $\text{CO}_2$  into  $\text{CO}$ , which does no harm when the chlorine is employed for producing bleaching-powder.

The apparatus patented by the Union Chemical Company of New York (Engl. pat. 23436, 1893) as usual contains an iron tank serving as cathode. The anodes are of retort-carbon, with holes drilled in their top ends, through which pass carbon pins, coated with paraffin or encased in glass tubes, serving for the electrical connexions. The anodes are placed vertically on an insulating base, resting on wire gauze at the bottom of the tank; they are covered by a stoneware bell for collecting the chlorine, which may be drawn off by an exhauster.

Hargreaves and Bird (Engl. pat. 18871, 1892; 5197 & 18173, 1893) employ cells with a horizontal porous diaphragm (described in Chapter XXX., specially treating of these), containing on the cathode side only so much liquid as penetrates through the diaphragm, or is introduced as a spray for the purpose of washing off the carbon. The anodes consist of carbon. The solution of salt is supplied at one side to the anode chamber, constructed of stoneware and situated above the cathode chamber, and the liquid is run away at the other side; the chlorine is carried away at the top. The liquid runs across the diaphragm and yields caustic soda on its lower side. The lower (cathode) chamber consists of a cast-iron tank with steam-pipe and outlet-pipe for the caustic solution formed. The steam introduced here constantly washes off the caustic soda from the diaphragm, and the heating produced also promotes the process. Instead of steam a spray of water may be applied, or else moist air or moist carbonic acid, *e.g.* from a hot-air engine; in the latter case, of course, carbonate or bicarbonate is produced. In order to prevent polarization, the cathode may be covered with metallic oxides, or with a catalytic substance, as platinum, in connexion with oxygen or a substance yielding oxygen. Their German patent, No. 83527, describes a cheaper form of the apparatus. The December number of the 'Journal of the Society of Chemical Industry,' 1895, contains a paper on this process, by Mr. James Hargreaves, with a very interesting discussion.

Blackmore (Engl. pat. 23913, 1893) employs three cells, two containing at first water, the third a solution of salt; the latter is

placed in the centre, at a lower level, and contains a smaller depth of liquid; it is divided from the lateral water-cells, containing the electrodes, by porous or "dialyzing" diaphragms, so that the electrolyte cannot get into these higher water-cells, which later on also contain a weak solution of the electrolyte.

Jorgensen's apparatus (Engl. pat. 5721, 1894) is U-shaped, with a porous diaphragm in the lower bend, and electrodes extending downwards within the limbs.

The Farbwerke vorm. Meister, Lucius, and Brüning (Germ. pat. 73651) introduce the electrolyte *between* the electrodes, in such manner that it divides into two streams, right and left, in a plane of at least the same surface as that of the electrodes, and is carried away from the outside of the electrodes. The liquid may be supplied by a set of pipes so that the division into two currents takes place only when issuing in the space between the electrodes, or else separately by two sets of pipes, one for each electrode. The latter is preferable, if the drawn-off liquid is to be introduced again into the decomposing cell, without separating the products of decomposition. In both cases two separated currents of liquid are formed, which move away from each other towards the electrodes. Thus, in fig. 199, the liquid runs from a reservoir into the cell, and under pressure through the small

Fig. 199.

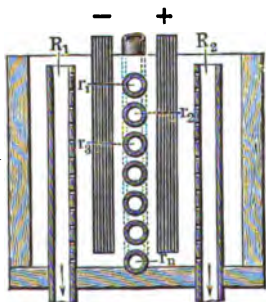


Fig. 200.

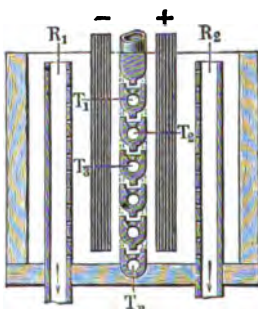
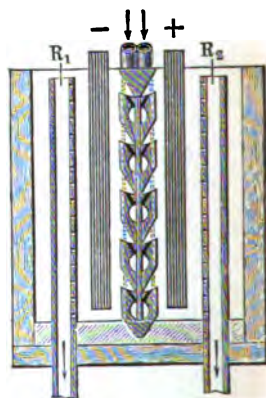


Fig. 201.



pipes  $r_1, r_2 \dots, r_n$ , arranged between the electrodes one above the other, and provided with openings pointing upwards to the right and left; it runs off through pipes  $R_1$  and  $R_2$ , arranged on the

outside of the electrodes, and pierced with many small holes all along. From these it flows into two tanks, is pumped into reservoirs placed on a higher level, and is again brought to the former concentration. Fig. 200 shows a similar arrangement with hollow troughs, provided with small holes all along. Fig. 201 shows an arrangement in which two separate sets of pipes are provided. The small pipes are arranged one above another as close as possible; the interstices may be filled up by osmotic layers. Preferably the electrolyte is run through decomposing cells placed in steps one above another.

The Société Outhenin Chalandre Fils et Cie. (Engl. pat. 15906, 1893) describes an apparatus in which the iron cathodes project horizontally into the partition towards the anode chamber. The cathode chamber is fed with water in order to avoid any contamination of the caustic liquor with common salt. The specification describes all details of the apparatus with great minuteness.

Hurter, Auer, and Muspratt (Engl. pat. 19791, 1893) arrange the anodes in a bell, below the lower edge of which at a certain distance plates of non-conducting material are fixed so that they project on all sides over that edge, and prevent the hydrogen given off at the bottom of the outer cathode vessel from penetrating into the anode chamber. [According to *Zschr. f. Elektrotechnik und Elektrochemie*, 1894, p. 301, Jabloschkoff had proposed a cell of exactly the same construction for the electrolysis of fused salts ten years ago.]

Drake (Engl. pat. 11644, 1894) surrounds a porous crucible, standing in an iron vessel, with amalgamated copper-wire gauze, serving as cathode. The solution of salt is placed in the crucible and water in the outer space.

Carmichael (Engl. pat. 8061, 1894) describes a number of conditions for electrolysis, which he formulates in not less than thirty claims.

Roberts (Engl. pat. 20111, 1892, and 13358, 1894) employs an iron vessel as cathode; the carbon anode is placed in a porous earthenware vessel filled with solid salt; a long tube provides a constant supply of more salt. On the outside there is, within a bag made of wire gauze or asbestos, a gelatinous diaphragm, consisting of ground coal, solution of silicate of soda, 25° to 80° Baumé, and 2 or 3 per cent. NaOH; the latter is to prevent the coagulation of the silica by the impurities of the coal.

Gall and Montlaur (French patent 240697) describe the following electrolytic apparatus:—In a trough are placed from end to end horizontal porous pipes; the anodes are arranged inside, the cathodes outside these pipes, and the current is thus efficiently divided. The liquid enters at one end of the tube from below, and the gas escapes through the dome-shaped top. Or else closed cylinders are employed as negative compartments, within which are placed vertical porous tubes.

Hulin (Engl. pat. 11587, 1894) employs porous electrodes, only one surface of which is active ("electrofilters"), the electrolyte being kept between them under pressure. On the passage of the current the ions migrate through the electrodes, caustic soda collecting in one and hydrochloric acid in the other of the outside compartments, the electrolysis requiring a voltage of only 1 volt [?].

Thofehrn (Engl. pat. No. 7994, 1894) employs an apparatus in which the Cl and H evolved during the electrolysis may be partly carried away mixed (*e. g.* to produce HCl), partly separate. For this purpose a screen is interposed between the two electrodes, which are arranged one above the other; below this screen a portion of the gases is caught and conducted outside the apparatus. According to the width of this screen, which is so constructed that it can be easily exchanged for another, more or less gas will be caught.

Solvay (Germ. pat. 80663) works *without separation of the two gases formed in electrolysis*, chlorine and hydrogen. The presence of hydrogen is not prejudicial to the absorption of chlorine by lime; if a continuous mechanical apparatus (p. 468) is employed, the danger of explosion is in this case very slight. He prefers a revolving drum, fixed in an inclined position, with screw-shaped ribs inside. The mixture of gases is rendered less explosive by adding to it the pure hydrogen remaining from a previous operation; in this case even ordinary bleaching-powder chambers may be employed. If hypochlorites are to be manufactured in the wet way, the mixture of H and Cl may be directly employed. The advantage is that in constructing the electrolytical apparatus there is no trouble in keeping it gas-tight outside the liquid.

Straub (Germ. pat. 73662) heats and cools the solutions in the bath itself by the electrodes. For this object either the electrode-plates are attached to closed frames, which are filled inside with

the electrolyte and dipped in hot or cold water; or else the electrodes are made hollow and the heating- or cooling-water is made to circulate inside.

Gautier (Engl. pat. 10032, 1894) provides means for cooling the electrodes so that the temperature of the cell may be kept down to that of the best working conditions. This is effected by causing the liquid to be electrolyzed to pass through pipes contained in the positive electrode, while the negative electrode is caused to revolve and is cooled by the circulation of water through it.

#### *Production of Sodium Sulphate and Chlorine.*

Parker and Robinson (Engl. pat. 2310, 1889) place in the anode space a half-saturated solution of  $\text{NaCl}$ , in the cathode space a solution of  $\text{FeSO}_4$ . On the passage of the current chlorine is produced at the anode, metallic iron and sodium sulphate at the cathode.

#### *Utilizing Nitre-Cake by Electrolysis.*

Darling (Engl. pat. 12316, 1895) places a solution of nitre-cake in the two outer (negative) cells of a tripartite trough, and a solution of brine in the central (positive) compartment. On electrolyzing the latter the sodium passes through the porous partitions into the outer compartments, thus converting the nitre-cake into normal sodium sulphate, and the chlorine gas escapes from the central cell in the usual way.

#### *Further Treatment of electrolytically obtained Solutions of Caustic Soda.*

The separation of electrolytically obtained  $\text{NaOH}$  from undecomposed  $\text{NaCl}$  is effected by Kellner (Engl. pat. 9347, 1892) as follows:—The solution is conveyed by a pipe into a “precipitating-apparatus,” in which it is boiled down in order to get the sodium chloride to crystallize out. The pasty mass thus obtained is put into a displacing apparatus, provided with a false bottom covered with wire gauze. A quantity of solution of sodium chloride is added, corresponding in volume to the caustic liquor mechanically retained by the salt. The displaced caustic liquor runs into another vessel, where it is again boiled down; the caustic liquor

retained by the salt separating here is again displaced, and this is continued until the necessary strength has been reached. Additions to this are made by patents Nos. 27541 and 25368, 1894.

Browne and Guthrie (Engl. pat. 8907, 1893) mix the electrolytically obtained caustic liquor with sodium bicarbonate from the ammonia-soda manufacture which has been deprived of ammonia and part of its  $\text{CO}_2$  by heating. The proportions are chosen in such a way that  $\text{Na}_2\text{CO}_3$  is formed. To this 2 per cent.  $\text{Na}_2\text{SO}_4$  and a little bleaching-powder is added (to oxidize any colouring-substances), the solution is brought to 26 per cent.  $\text{Na}_2\text{CO}_3$ , allowed to settle and to crystallize by cooling.

Häussermann mentions, as a matter of course, that the electrolytically obtained liquor is concentrated in multiple-effect pans, preferably such as admit of mechanically withdrawing the salt crystallizing out. The liquor, being thus concentrated to spec. grav. 1.45, is finished in an ordinary caustic pot (comp. above, p. 652).

Solvay & Co. (Engl. pat. 14987, 1894) precipitate from the electrolyzed solution the chloride by means of a solution of caustic soda of 77° Twaddell. The magma thus obtained, which is difficult to filter, is placed in a steam-jacketted vessel with a perforated false bottom and heated to 100° C. (which is essential). A saturated solution of soda is then introduced at the top, and this mechanically displaces the caustic liquor, which is drawn off at the bottom.

## II. PROMOTION OF THE ELECTROLYSIS OF SODIUM CHLORIDE BY CONVERTING THE SODIUM HYDRATE INTO CARBONATE OR OTHER COMPOUNDS.

The electrolysis of an aqueous solution of sodium chloride does not proceed to a complete decomposition into  $\text{NaOH}$  and  $\text{Cl}$ , because, to begin with, the current acts also upon the sodium hydrate formed. It is true that the heat of formation of  $\text{NaOH}$  (in aqueous solution) from  $\text{Na}$ ,  $\text{H}$ , and  $\text{O}$  is 112.1, against only 96.2 for  $\text{NaCl}$  in solution; the contrary assertion made in the German patent of Hermite and Dubosc, No. 66089, is quite wrong, as they calculate with the heat of formation of  $\text{Na}_2\text{O} = \frac{155.2}{2}$ .

It is therefore wrong to say, as they do, that a current whose



tension suffices for decomposing  $\text{NaCl}$  must also decompose the product, since this product is not  $\text{Na}_2\text{O}$ , but  $\text{NaOH}$ . Still it is not possible to regulate the current so that it can decompose only  $\text{NaCl}$  but not  $\text{NaOH}$ ; this by itself is a good reason for approving of the efforts to remove the  $\text{NaOH}$  formed as quickly as possible from the reach of the electrolytic force.

Most of the proposals in this direction tend to convert the  $\text{NaOH}$  by a supply of  $\text{CO}_2$  into carbonate or bicarbonate, which are insoluble in concentrated solution of common salt and are thus withdrawn from the action of the current. But we shall see that this can be attained also in other ways.

W. Hempel (Ber. deutsch. chem. Ges. 1889, p. 2475) starts from the fact that the electrolysis of chlorides cannot be completely achieved, because the products, after accumulating to a certain extent, are themselves decomposed by the current. This is not so if substances of small solubility are formed. This fact had been previously utilized for the production of potassium chlorate [not of sodium chlorate, as he erroneously adds, this salt being too soluble], and Hempel endeavoured to utilize the small solubility of sodium carbonate and bicarbonate in saturated solutions of  $\text{NaCl}$  for the same purpose. (He was not aware that Marx had proposed this before him, as we shall see.) He constructed an apparatus in which  $\text{CO}_2$  could be introduced during the process, and he states that the work can be conducted so as to form on the one hand chlorine, on the other crystallized sodium carbonate. [From his description we cannot see that he had convinced himself of the latter fact; probably by his process principally bicarbonate is formed, and a corresponding amount of  $\text{CO}_2$  is consumed, as supposed by Marx from the outset.] He rightly points out that the action of the "liquid diaphragms" patented by Marx must be very imperfect. He found that clay cells were too quickly stopped up; parchment-paper and animal skin do not resist the chemical action; asbestos, in the shape of ordinary asbestos cardboard, after a few days became soft and useless. But the latter material turned out to be excellent when used in such manner that no deformation could take place. Figs. 202 and 203 show the arrangement of Hempel's laboratory apparatus, which, as he thinks, could be easily carried out on the large scale with an iron cathode vessel. The cathode is a perforated piece of sheet-iron, the anode a thin perforated carbon disc. The holes are

about 4 millim. wide and bored in an upward slanting direction, so that the gas-bubbles can easily escape. Both electrodes are circular; the margin is not perforated for 3 centimetres, so as to allow of making a tight joint there. The diaphragm is a sheet of ordinary asbestos cardboard, placed between the iron and carbon disc. Thus the electrodes can be brought within 1 millimetre, which greatly reduces the resistance, and the asbestos is so well supported that it is never torn up by the liquid; after eight days and nights continuous work it seemed to be quite intact.

Fig. 202.

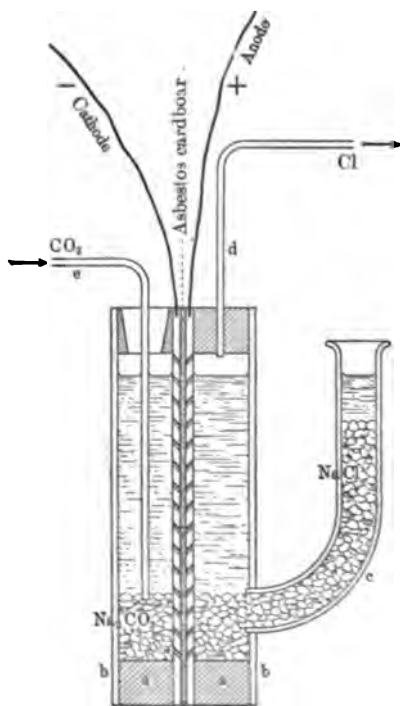
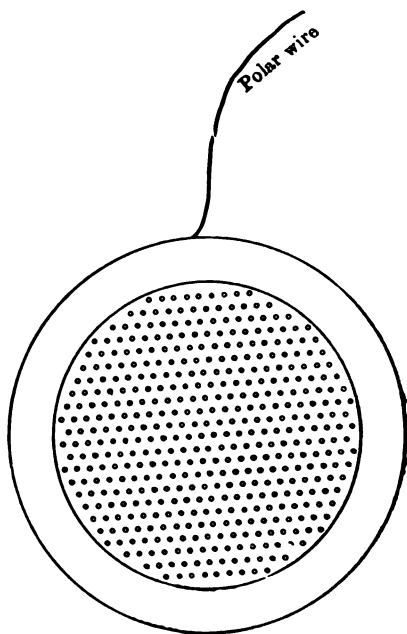


Fig. 203.



Chambers are formed on each side of the electrodes by porcelain rings *a* and glass discs *b*, with india-rubber washers to make the joints, the whole being kept together by screw clamps not shown in the diagram. In the glass disc belonging to the anode

chamber a hole is drilled in which, by means of an india-rubber ring, a wide glass tube *c* is fixed. The glass pipe *d* carries away the chlorine; pipe *e* serves for introducing the  $\text{CO}_2$ . Through *c* fresh sodium chloride is added; the water consumed is also replaced. The sodium carbonate is from time to time removed from the cathode cell, and the apparatus works quite continuously. It is preferable to work at the ordinary temperature, on account of the greater solubility of the sodium carbonate at higher temperatures, although these would be better for the electrical decomposition. The apparatus requires a tension of 3.2 volts for decomposing the  $\text{NaCl}$  [?] and 2.5 volts for overcoming the polarization, together 5.7 volts. With a current of 1.73 ampères, produced by ordinary Bunsen cells, 0.930 gram chlorine per hour was produced. Calculating a H.P. = 680 watts, a dynamo would have produced 64.5 grams chlorine and 259.8 grams  $\text{Na}_2\text{CO}_3$ , 10  $\text{H}_2\text{O}$  per horse-power hour.

Hempel's paper has no direct practical application, since it is economically wrong to convert a more valuable product, caustic soda, by means of carbonic acid (always costing something, even if employed as lime-kiln gas) into a much less valuable product, viz., soda crystals or crude bicarbonate. Nor is his apparatus fit for reproducing on the large scale; the anode chamber cannot be made of iron, and any other material is not easily applicable for the lateral position in his apparatus. The object could be attained by placing in an iron tank, serving as cathode chamber, *two* such combinations of iron and porcelain plates as used by Hempel, with the porcelain part inside and the iron outside; the central space would then be the anode chamber. His arrangement of an asbestos diaphragm, with a very small distance between the electrodes, appears to be very good and easily carried out on the large scale. The voltage he observed was certainly excessive, and would not allow of economical work, but on the large scale it would be quite different.

Marx (Engl. pat. 6417, 1887; 2367, 1888) also applies the saturation of the  $\text{NaOH}$  by  $\text{CO}_2$  in order to exclude the action of the current on the former. Another part of his invention, considered by him as very important, is the separation of the anode and cathode space by a layer of liquid, prevented by a grate or tissue from quickly mixing with the other liquids, which greatly

diminishes the resistance. Laterally pierced supports contain the common salt, which gradually dissolves and keeps the liquid always at the same concentration. In the cathode chamber  $\text{CO}_2$  is introduced by a pipe pierced with many holes, in such quantity that the soda is precipitated as bicarbonate, which is removed by a conveying screw and a chain of buckets. The liquid employed as 'liquid diaphragm' is a solution of salt with lime suspended therein, which prevents the passage of  $\text{CO}_2$  into the anode space. The sodium carbonate is to be decomposed in the usual manner, or preferably to be converted into carbonate by quickly mixing it with caustic liquor; in this case the carbonate is not at once dissolved, and can be separated from the mother liquor by a centrifugal machine [this would yield a very impure product!]; or it is converted by a milk of magnesia into a double salt, which is afterwards decomposed by boiling and evaporation.

Later on, Marx describes a tank with two inner osmotic diaphragms; within this osmotic chamber the chlorine and caustic soda, entering by diffusion, are to combine to a bleaching-solution of sodium hypochlorite; after being used for bleaching purposes, and converted thereby into chloride, it is re-conducted into the anode chamber. Chlorate can also be obtained in this way in the osmotic chamber in a solid state.

In his last patents (No. 6264, 1890; 3738, 1891) Marx describes a peculiar arrangement of the decomposing-vessel, in which all diaphragms are avoided by placing the electrodes one above another, leaving above and below each electrode an electrically inactive space. Each electrode of the lower series is placed just below the space between two of the upper electrodes, and *vice versa*. The spaces between the equivalent electrodes are filled with a chemically inactive insulator, so that the liquid can only touch the electrodes in a thin lateral layer. Since this arrangement is novel and interesting, it is shown here in figs. 204 and 205. *a* are the lower electrodes, connected one with another like the teeth of a comb, and at the same time serving as containing vessel; they are separated by insulating straps *b*, so that the liquid is able to flow, but no electrolytical action can take place between the electrodes *c* suspended above in the junctions. The upper electrodes *c* rest by means of projections *d* on the bearers *e*, which allow of their being adjusted; they consist of single rods, whose interstices *c'* communicate with

a common chamber *f*, possessing outward openings *g*. The insulating layer *h* between the upper electrodes possesses also outlet openings *i*. The electrodes *a* with the insulating walls *b* rest in a

Fig. 204.

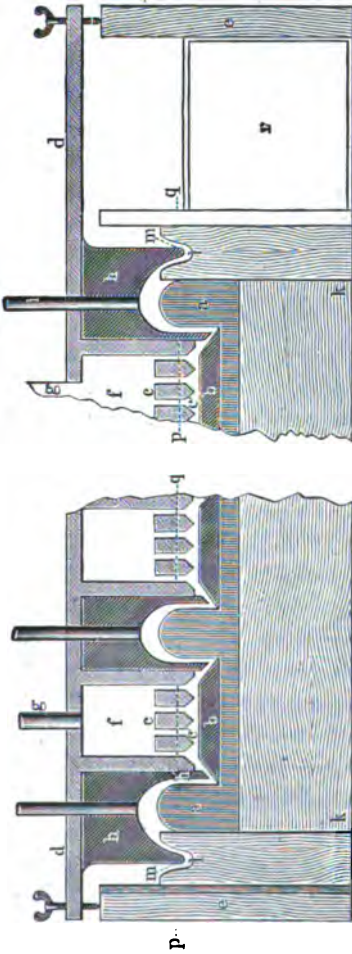


Fig. 205.



frame, provided with a furrow *l* running all round; this furrow is filled with water, and serves as hydraulic lute for the upper section of electrodes, *c, f, h*, fixed in the frame *m*. The electrodes *a* are so arranged that the electrolyte can run backwards and forwards, and ultimately issues outside, during which the insulating walls *b*

are washed over by the liquid reaching up to the dotted line  $p q$ . The hydrogen given off at the cathodes is carried away by  $i$ ; the chlorine evolved at the anodes  $c$  and collecting in the chamber  $f$  is carried away by  $g$ , the latter by means of an aspirator. This action, as well as the fact that the chlorine has to pass through a very thin layer of liquid, gives it very little opportunity for being re-absorbed. The projections  $h'$  of the insulating mass prevent, without a diaphragm, any mixture of the gases evolved at  $a$  and  $c$ . In spite of this arrangement there is still a slight reunion of chlorine and alkaline hydrate, which causes a loss of chemical substance, and in consequence of polarization an extra consumption of current. In order to counteract this, an apparatus  $r$  is laterally attached to the decomposing vessel; it is shown in fig. 205 in section at right angles to the plane of the paper. The electrolyte runs through the pipe  $o$  into the stand-pipe  $o'$ , open at top and bottom, from this into tank  $s$ , and from this through the overflow  $t$  over the inclined plane  $u$  into tank  $s'$ , from which it flows by pipe  $n$  into the next electrolytic cell, and from the last of these into the place where it is consumed. The inclined plane  $u$  is interrupted by the cross ribs  $u'$ , which detain the liquid and produce a good mixture. The top of the apparatus is closed by the cover  $v$ , which is pierced by the necks  $v'$  and  $v''$ , by which carbonic acid is passed in, being prevented from escaping by the hydraulic lutes at  $s$  and  $s'$ . The  $\text{CO}_2$  converts the  $\text{NaOH}$  into carbonate, and produces from the hypochlorite free  $\text{HOCl}$ . On flowing into the next electrolytic cell the decomposition of the chloride progresses, the free  $\text{HOCl}$  being converted into hypochlorite by the newly formed alkali. The liquor issuing from the last apparatus is treated with more  $\text{CO}_2$ , in order to precipitate the alkali; by adding salt it is brought to the initial concentration, and is again submitted to electrolysis. If a bleach-liquor is to be prepared, the chlorine is not removed by aspiration, which promotes the formation of hypochlorite; on subsequent treatment with  $\text{CO}_2$  much  $\text{HOCl}$  is formed, and after carrying out the bleaching-process this  $\text{HOCl}$  is always regenerated in the electrolytic bath.

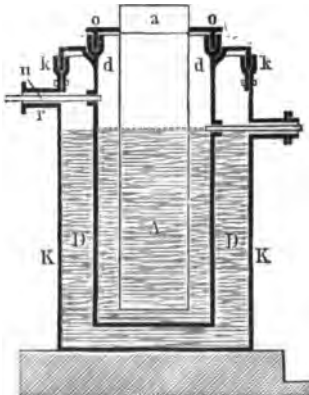
Craney (Engl. pat. 9979, 1894) also describes an apparatus for electrolyzing a solution of  $\text{NaCl}$  while passing  $\text{CO}_2$  through the liquid.

Spilker and Löwe (Engl. pat. 14494, 1887) believe that caustic

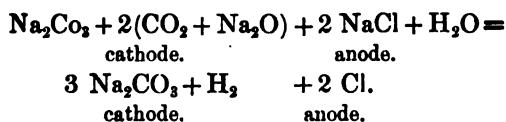
alkali, "almost entirely free from chloride," and free chlorine are obtained as follows:—The alkali within the iron cathode vessel is continuously increased by keeping the liquid within the anode space (formed by a porous earthenware vessel) alkaline by means of hydrated lime or magnesia. Subsequently, together with Knöfler (Germ. pat. 49627), they patent the apparatus shown in fig. 206.

The cathode is formed by the iron vessel K, coated with lead; in this are suspended porous earthenware cells D with the anodes A. A number of such baths are placed in steps, with the overflow pipes *r*, through which pass also the gas-pipes *u* coming from the anodes. The hydraulic lutes at *k* and *d* make a gas-tight joint at the top. The anode cover *o* is pierced for the anode A, which is cemented in it so as to be gas-tight, and projects far enough to be connected with the conductor of the current.

Fig. 206.



Later on, Spilker and Löwe found it preferable to keep caustic only in the anode space; the cathode space is to contain a "neutral or slightly acid" hot solution, which is produced by a current of carbonic acid. If the anode space contains NaCl and the cathode space  $\text{Na}_2\text{CO}_3$ , the decomposition takes place as follows:—



The anode space loses its sodium by osmosis, with evolution of chlorine; the Na in the cathode space forms neutral carbonate with the sesquicarbonate, with evolution of hydrogen. In the beginning of the decomposition the bulk in the anode space decreases, that in the cathode space increases. At a certain rate of concentration, viz., when the proportion of the carbonate is equivalent to that of the chloride, the concentration of the cathode space, produced by  $\text{Na}_2\text{CO}_3$ , no longer increases by electrolysis, only the bulk increases, exactly corresponding to the amperage—

if, for instance, a solution of 15·5 per cent.  $\text{Na}_2\text{CO}_3$  is in the cathode space, and a solution of 18 per cent.  $\text{NaCl}$  in the anode space. On the large scale this is to be carried out so that a number of baths are placed in steps, the anodes being connected with anodes, the cathodes with cathodes. Into the cathode space of the top bath a current of carbonic acid is continuously introduced, into the anode space of the same bath a stream of fresh salt solution, and from the bottom bath a continuous stream of carbonate flows out, which is worked for crystal soda, while the chlorine issues from the cathode space of the same bath.

Their patent No. 47592 is carried further by Germ. patent No. 64671, taken out by the Vereinigte chemische Fabriken, Leopoldshall. If as anode liquid potassium chloride is employed, made alkaline by lime &c., as cathode liquid caustic potash, the parchment-paper diaphragms are quickly spoilt by hypochlorite. If, however, we add to the anode liquid from the first, besides  $\text{KCl}$ , about 2 per cent. calcium or magnesium chloride, there is soon formed on the parchment-paper a firmly adhering, uniform coating of lime, magnesia, and oxychlorides, which counteracts the action of the hypochlorite. If the coating has reached a thickness of  $\frac{1}{3}$  inch, the supply of lime to the anode liquor is reduced by about 20 per cent., whereupon the coating retains the same thickness; it thus forms a new porous diaphragm of very slight electrical resistance. The cells are constructed as follows:—Iron frames about 1 centimetre thick, with the slots *a*, *k*, *b*,

Fig. 207.

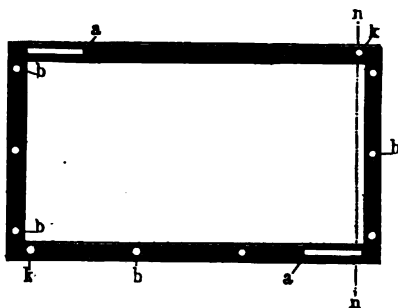


fig. 207, confine a cathode cell. On these perforated sheets of iron, provided with similar slots, are so placed that the free



parts of the frames are covered; upon this are placed one or more sheets of parchment-paper, then a correspondingly cut-out anode frame, 6 centim. thick, open at top, again parchment, perforated sheet-iron, cathode frame, perforated sheet-iron, and so on. Through holes *b* pass iron rods, with screw ends for compressing the whole apparatus. Holes *a*, *k* form four channels for the inlet and outlet of the anode and cathode liquor. The layers of perforated sheet-iron act as cathodes, the frames upon which they are pressed serve for conducting the current, so that the whole consists of closed cathode cells and anode cells open at top. In these openings the anodes are placed, and if gases are given off there (in our case, chlorine), the joint is made air-tight. The perforations of the sheets are intended to allow the liquor to circulate and the hydrogen to escape.

Fitzgerald (Engl. pat. 9799, 1892) also proposes adding to the electrolyte in the anode cells an insoluble basic oxide as lime, or perhaps magnesia or zinc oxide, in order to combine with the chlorine and to permit employing "lithanode" as anodes (comp. Chap. XXX.).

Parker and Robinson (Engl. pat. 14199, 1888) work without porous cells or diaphragms. During electrolysis  $\text{CO}_2$  is introduced under pressure, which decomposes the first-formed hypochlorites, producing carbonate and free chlorine, which is easily separated from the carbonic acid (?).

A later patent of Parker's (No. 23733, 1892) returns to porous diaphragms. The electrolyte is to be heated to prevent the absorption of chlorine. The  $\text{CO}_2$  is to be introduced into the cathode chamber in the form of bicarbonate. The anodes are to be prepared by mixing anthracite (or coke from anthracite) with graphite and pitch, and compressing with or without application of heat; in the former case embedding them in graphite so as to produce a film of it on the surface.

Kellner (Engl. pat. 20713, 1891) describes the following process:—A heated saturated solution of sodium chloride circulates in two separate, quick streams through an electrolytic apparatus. The stream which passes the anodes contains a little addition of sulphuric acid or sodium sulphate, and on leaving the apparatus is passed through a vessel filled with solid  $\text{NaCl}$ , so as to be again saturated before returning to the anodes. The other stream, which passes the cathode, after leaving the apparatus is

simultaneously exposed to cooling, to contact with solid salt, and to the action of  $\text{CO}_2$ , by which the soda is converted into carbonate and precipitated, whereupon the solution returns to the cathode cells. The electrolysis is carried out in a series of frames, R, figs. 208 & 209, in which the electrodes are fixed and which are separated by diaphragms; in their upper portions they possess channels  $g, g_1$ , which are connected by passages  $h, h_1$  with the channels by which the electrolytes circulate; the evolved gases escape separately through  $g$  and  $g_1$ . The diaphragms D consist of permeable tissue or of clay, the pores being filled with a jelly

Fig. 208.

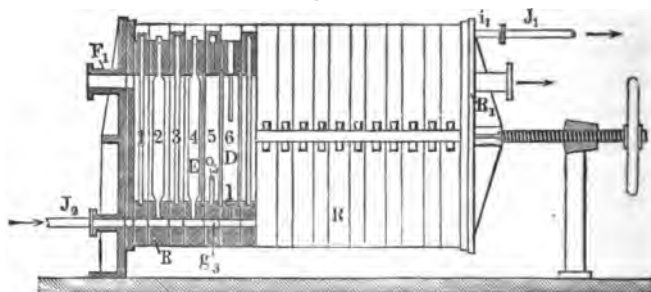
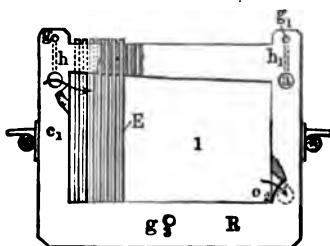


Fig. 209.



mixed with some  $\text{NaCl}$ . This obviates an injurious mechanical diffusion from one cell into another, and also promotes the circulation of the ions. The electrodes are prepared by mixing ground retort-carbon with a thick solution of wood cellulose in zinc chloride, which is kneaded to a paste, moulded, washed, and heated in a muffle, after which process it is impregnated with mineral oil and again heated. Or electrodes are employed whose pores are

stopped up with lead peroxide, obtained either by coating them with a mixture of litharge and ammonium sulphate, or by boiling them in a saturated solution of lead acetate and electrolytically transforming this into peroxide.

Hermite and Dubosc (Germ. pat. 66089), on the erroneous assumption that more molecular force is required for decomposing NaCl than NaOH (p. 674), cause the  $\text{Na}_2\text{O}$  produced, immediately after its formation, to enter into a sodium compound whose heat of formation is above that of NaCl, as they believe that in this case, the electromotive force being constant, the new compound is no longer influenced by the current and the NaCl remains the only electrolyte. For this purpose they add to the bath *gelatinous hydrate of alumina*, which combines with the soda, as it is formed, to sodium aluminate. This is afterwards decomposed by  $\text{CO}_2$  and the liberated alumina is used as above.

Parker and Robinson (Engl. pat. 4920, 1893) withdraw the NaOH formed by electrolysis from the further action of the current in the shape of *soap*, which does not prevent the continued electrolysis of NaCl. For this purpose they add a fatty acid (oleic or stearic) or a neutral fat; the soap formed, owing to its low specific gravity, rises to the surface and is removed, in order to be used as such or to be converted by  $\text{CO}_2$  into  $\text{Na}_2\text{CO}_3$  and free fatty acid.

## CHAPTER XXVI.

III. ELECTROLYSIS WITH SEPARATION OF THE ALKALINE METAL  
BY A MERCURY CATHODE.

A SPECIAL group of electrolytical soda- and chlorine-processes, which has attracted great attention during the last few years, is carried on so that the secondary reaction  $\text{Na} + \text{H}_2\text{O} = \text{NaOH} + \text{H}$  does not take place at the cathode itself, but the sodium, as it is formed, is protected from the action of water by being at once taken up by mercury in the shape of an amalgam which is decomposed in another place. Thus the drawback of producing caustic liquor containing a large excess of NaCl is avoided (p. 634).

Already, in the beginning of this century, Davy had employed a mercury cathode in his classical research on the preparation of the alkaline metals, in order to secure them from dissolution by the electrolyte.

The electrolysis of NaCl with employment of a mercury cathode, in which the sodium is dissolved, is also mentioned by Nolf in the application No. 4349, 1882, which did not proceed beyond the provisional protection.

We find the mercury cathode again in Hermite's patent No. 3957, 1888, which does not yet aim at the production of free chlorine. Cloth or yarn to be bleached is placed in a tank, at the bottom of which is a layer of mercury, electrically connected with the negative pole of a source of current, the anodes being made of platinum or carbon. The electrolytes are chlorides of the alkaline or earthy-alkaline metals; according to patent No. 3956,

1888, also sulphates or caustic alkaline, in which case ozone is given off at the anode. The alkaline metal formed at the cathode is taken up by the mercury, and on interrupting the current, or in case of a short circuit, is decomposed by water. In this shape the process was evidently not yet practicable.

Later on Hermite and Dubosc (No. 21957, 1891) work without a porous diaphragm and employ a moving mercury cathode, which takes up the sodium (or potassium) as amalgam and at once withdraws it from the decomposing action of water by means of bisulphide of carbon; afterwards the amalgam is decomposed in a separate vessel into caustic soda and mercury. Fig. 210 shows their apparatus.

The solution of NaCl is placed in the tank C, in the centre of which is a conical cathode, P, P, of amalgamated copper, on which mercury flows in a thin stream from vessel G. P, P are the cathodes, consisting of two parallel sheets of platinum. The amalgam, whose percentage of sodium depends upon the intensity of the current and the rate of the feed, collects in the spouts H, H, leading through pipe T to an outer vessel F; the overflow *t* keeps the amalgam always at one level in H, H. A layer of bisulphide of carbon, S, floating on the amalgam, prevents its contact with the aqueous liquid. If the current is acting and the feed of mercury put on, the amalgam arrives in H, H, where a separation takes place; lighter amalgam remains at the surface and runs off through *t* into the vessel E, filled with water; the bend of *t* has the effect of allowing only amalgam to flow away. The mercury not changed into amalgam sinks to the bottom of H, H and runs through U into F; the mercury formed in E by the decomposition of the amalgam with water runs also into F through V. From F the mercury is brought into G by a chain of buckets I, J.

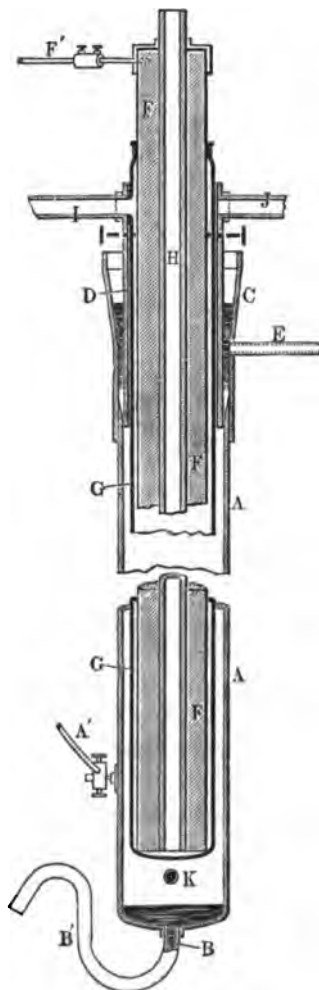
Atkins and Applegarth (Germ. pat. 64409) describe the following arrangement for a continuous flow of mercury across the cathode (fig. 211):—

A metal cylinder A, amalgamated inside, is provided with a bottom outlet B, ending in a tap or a siphon B'. At the top A is enlarged, and there receives the lower end of a second cylinder, D; there is, however, a small annular space left, through which mercury gets by pipe E on to the amalgamated inside of A, and flows down comparatively slowly, until it runs off at B. A forms



a cathode chamber with the electrical conductor A', and is filled with solution of salt. In the centre is the carbon anode F, surrounded by the hose G, closed at bottom, consisting of a dense tissue of hemp, treated with silicate of soda for its better conservation. The conductor F' connects the anode with the dynamo. The anode consists of a pipe H, upon which carbon rings are placed. The solution of NaCl is conveyed through H to the bottom of G, and on gradually rising round the outside of F it is electrolyzed. Most of the sodium passes through the sides of the hose to the cathode A; the remaining solution passes off at the top through I, together with the chlorine, and can be used over again after being brought up to strength. The caustic-soda solution in cylinder A can pass away through J, together with the hydrogen; at the opposite end of the cathode cylinder water is let in through K, in order to take the place of the caustic solution. Instead of the hemp hose a diaphragm of ordinary caustic material can be employed. In order to retard the downward flow of the mercury the cathode may be provided with ribs. The specification describes also other arrangements for spreading the mercury in a thin layer over the cathode.

Fig. 211.



Greenwood (Engl. pat. 5999, 1891) produces sodium amalgam in the apparatus known from his former patents (p. 658), by providing a supply of mercury for the cathode cell.

The most important of the mercury processes is Castner's (Engl. pat. 16046, 1892). He employs a moving mass of mercury between the anode and cathode chamber, the electric current being

made to pass from the anode through the mercury to the cathode, so that the sodium produced immediately dissolves in the latter; this prevents polarization and admits of employing a great current-density. If in the cathode chamber water is admitted at the same time, caustic soda is produced. The mercury should from the first contain a little sodium, and this percentage must be always kept up in a proper manner. According to patent No. 10584, 1893, the process is made continuous by mechanically rocking the cell divided into two compartments, so that the mercury is alternately in that chamber where it takes up the sodium as amalgam, and in the other chamber where the sodium is extracted as NaOH. The depth of the mercury bath is  $\frac{1}{2}$  inch; therefore the front end of the cell need be moved only  $\frac{1}{2}$  inch above or below the horizontal plane. This apparatus is shown in figs. 212 & 213. A is the decomposing-tank with three compartments, the back end being supported by adjustable knife-edges B. These

Fig. 212.

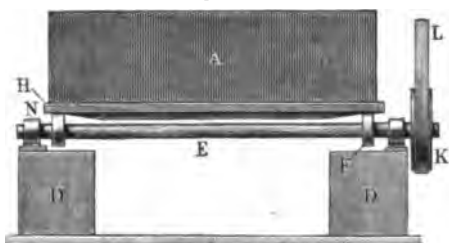
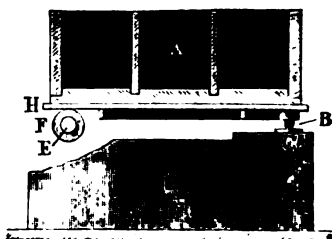


Fig. 213.]



rest upon metal plates C, and the latter on a frame D. The front end of A rests on excentres F, attached to a shaft E. These excentres lean against the metal plate H, and thereby against the bottom of the cell. The shaft E revolves in the bearings N N and is geared by K and L.

The Chemical Trade Journal, 1894, xv. p. 211, contains the following statements by Castner himself on his process. The reunion of the products of decomposition to hydrochlorite is excluded; the carbon anodes therefore keep perfectly; there is no porous diaphragm, and the solution of caustic soda is absolutely pure and free from chloride. The plant at Oldbury contains 30 cells in two parallel rows of fifteen each. The current is taken from a Crompton dynamo, having an output of 1100 amp. at



60 volts, the current being divided so as to apply 550 amp. to each row. Of the circuit of 15 cells connected in series, 14 are always in use, one being held in reserve. At that time (end of September) the cells had been running continuously since August 14th. Detailed results are given of one week's run (from September 18 to 24), checked by reliable measuring instruments, the daily average being 571 amp. and 55.1 volts, with an output of 3080 lbs. caustic-soda solution of spec. grav.  $1.204 = 560.1$  lbs. NaOH, equal to an efficiency of 88.5 per cent. Each cell had yielded 40 lbs. NaOH per diem, with an average E.H.P. of 3.01 or 3.55 I.H.P. The 28 cells therefore furnish 1120 lbs. NaOH and 930 lbs. chlorine. The analysis of the finished caustic was 95.58 per cent. NaOH, 2.37 per cent.  $\text{Na}_2\text{CO}_3$ , 0.05 per cent. NaCl = 78.30 per cent. Liverpool test.

The statements certainly refer to a very short period, and nothing is said about loss of mercury, &c.; but from other sources it would appear that Castner's process is in fact working very well, and that the tension required is only 4 volts, a 20-per-cent. solution of pure NaOH being obtained.

Further details are given in the *Engineering and Mining Journal*, September 22, 1894, p. 270. The cells are divided into three compartments. The two outer ones contain the solution of sodium chloride and the carbon anodes; the central compartment contains the caustic-soda solution and an iron cathode. The solution of salt circulates continuously through the two outside compartments and then passes into a vessel where it is again saturated with fresh salt, replacing that decomposed by electrolysis. The chlorine escapes from each of these into a large main; the sodium amalgam in consequence of the rocking motion flows into the central compartment, where it now serves as anode, the current going to the cathode, and the sodium passing into solution as NaOH. The energy stored up in the sodium assists the electrolytic process. Every hour a certain quantity of water is admitted into the central compartment, so that a corresponding quantity of caustic-soda solution is made to overflow into a main connected with all the cells. Every cell is therefore in communication with four mains—for feeding concentrated solution of salt, for the outlet of the electrolyzed solution into the saturating vessel, for taking away the chlorine, and for taking away the caustic liquor. The cells are worked in series, and

every one of them can be put out of series as desired. The high electrical efficiency of 88–90 per cent. is principally explained by the fact that the sodium is removed from the mercury by electrolysis immediately after its formation, so that the mercury rarely contains more than 0·02 per cent. Na. Hypochlorites are not at all formed; the small loss of electrical energy is not caused by a combination of chlorine with caustic soda, but by recombination with sodium. Owing to the absence of hypochlorites the wear and tear of the cathodes (which are obtained by a special process) is scarcely perceptible. By means of that process even ordinary compressed coal or retort-carbon may be employed. The low E.M.F. (4 volts with 550 amp.) is explained by the non-accumulation of sodium in the amalgam, and by the close approach of the electrodes, which nearly touch. Each cell, 6 feet long, 3 feet wide, and 6 inches deep, decomposes per day 56·5 lbs. salt, and produces 38·5 lbs. NaOH and 34·5 lbs. chlorine, with an expenditure of 3·5 I.H.P. The caustic liquor contains 20 per cent. NaOH, and by direct evaporation yields caustic soda of 99·5 per cent. The chlorine-gas contains 95–97 per cent. Cl and 3–5 per cent. H. The action of the cells is automatic and requires hardly any supervision; their construction is so simple that a cell can be put out of series, cleaned, taken to pieces, put together, and set to work by two men in less than two hours. Taking the efficiency at 88 per cent. we obtain the following values:—

Each cell decomposes per hour...	1058	grams	NaCl.
„ produces „	724	„	NaOH.
„ „ „	642	„	Cl.
„ decomposes in 24 hours	56·5	lbs.	NaCl.
„ produces „	38·5	„	NaOH.
„ „ „	34·25	„	Cl.
Actual electrical horse-power per cell.....	3.		
„ indicated „ „ .....	3·5.		
Salt decomposed per ampère hour .....	1·92	grams.	
„ „ „ watt.....	0·48	„	
„ „ „ I.H.P. per hour .....	295	„	
Caustic soda produced per I.H.P. per hour...	209	„	
Chlorine „ „ „	183	„	
Salt decomposed „ in 24 hours	16·0	lbs.	
NaOH produced „ „	11·0	„	
Cl „ „ „	9·8	„	

According to the 31st Alkali Report, p. 66, the inventor states the loss of mercury = 5 per cent. per annum.

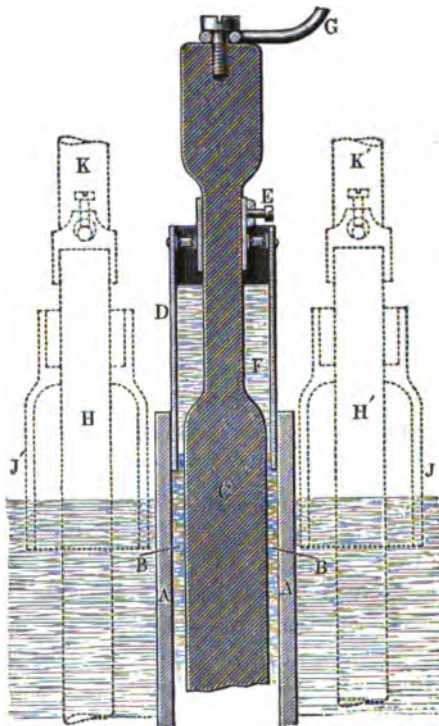
According to the prospectus of "The Castner-Kellner Alkali Company," as advertised in the papers in October 1895, a limited company had been formed which had taken over the Castner patents from the Aluminium Company (Lim.) and the Kellner patents from Messrs. Solvay & Co., and which seems to have devoted itself especially to the former. The prospectus states that the experimental factory at Oldbury, working with 100 H.P., had been in successful operation since August 1894, with an electrical efficiency of 88 to 90 per cent., producing a 20-per-cent. solution of almost chemically pure caustic soda. It was intended to lay out works up to 4000 H.P., manufacturing  $18\frac{1}{2}$  tons of 77 per cent. caustic soda and 40 tons of bleaching-powder *per diem*. The prime cost of the caustic was not expected to exceed £4 5s., and that of the bleaching-powder £3, both inclusive of packages. [This prospectus has been very adversely criticized, *e. g.*, in Chem. Tr. Journ. xvii. p. 271.]

Sinding-Larsen (Engl. pat. 13499, 1894) describes an apparatus consisting of a large vessel, covered at the bottom with mercury serving as cathode; a bell dips into this, within which the carbon anode and a chlorine exit-pipe are fixed. If the sodium amalgam formed at the cathode is to be recovered as such, the mercury outside the bell is covered with petroleum. The solution of salt rises below the bell in the centre of the cathode cell through a pipe reaching to the surface of the mercury; the liquid then overflows sideways from the bell. Another patent (No. 14910, 1894) mentions that the walls in contact with mercury are amalgamated, so that no liquid can find its way between them and the mercury, and that the anodes are made to revolve, in order to prevent the adhesion of gas-bubbles to their active side.

Kellner (Engl. pat. 17169, 1892) forms the cathode of a thin vertical layer of mercury, separated from the anode space, which contains the electrolyte, by electrically conducting partitions; during electrolysis water is constantly running over the mercury, while the gases escape from the anode space. The mercury takes up the sodium, and at once gives it up to the water, NaOH and H being formed. The following arrangement is stated to be useful and durable in actual practice:—The partitions A, fig. 214, which contain the mercury and separate it from the anode space, may

consist of porous earthenware, of asbestos cardboard impregnated with gelatine and resting on a perforated slate slab, or of two alternately perforated slate slabs with an interposed layer of glass and slag-wool, starch and coal, previously dipped in concentrated caustic solution or boiling water. In order to employ as little mercury as possible (shown at B), there is a cast-iron displacing

Fig. 214.



body C, which holds the mercury in a thin layer, and at the same time the reaction vessel D at a definite height. The latter consists of a frame open at top and bottom, dipping into the mercury to the depth set by the position of the screw E; water is introduced into the inner space F. The mercury is either directly or indirectly connected by C with the negative pole G. The anodes H H' consist of any refractory materials; they are supported by the bell-shaped frames J, J', and the gas is taken away by K, K'.

Fig. 215 gives a section, fig. 216 an elevation of the apparatus

Fig. 215.

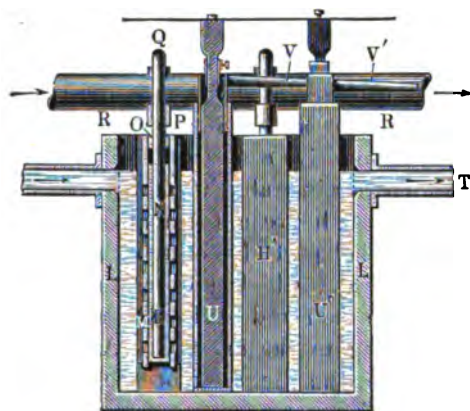
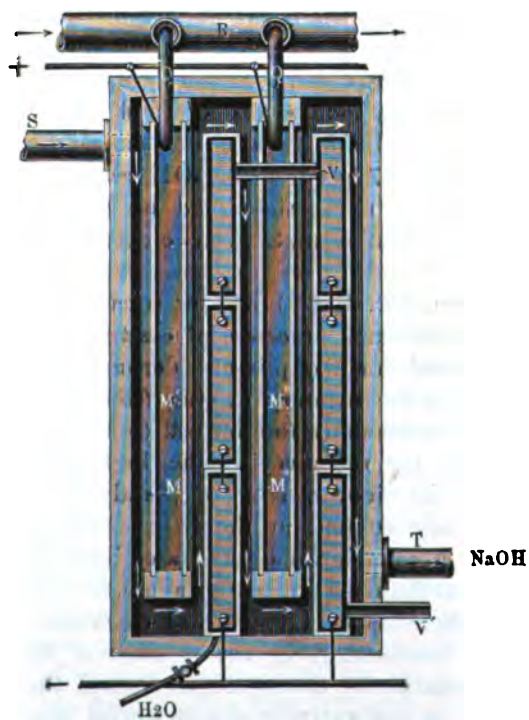


Fig. 216.



employed in practice. L is a wooden watertight trough; H, H' the anodes, consisting of a frame in which are placed plates M, M', made of slate (or porcelain or stoneware), with large holes, the space in between being filled with ground coal, into which the current is conducted by the carbon rods N, which are at O fixed in the frames by means of asphalt poured in, and at P are connected with the positive conductor. This is done by means of a strip of lead connecting all the carbon rods; as the conductivity of the junction between them quickly suffers from the action of the chlorine, that part of the carbons between O and P is freely exposed to the air, which prevents moist chlorine from penetrating between carbon and lead. On each anode there is a chlorine-pipe Q, leading to the main R. At S enters the electrolyte, which travels in the direction of the arrows through the maze between the anodes and cathodes, and at T leaves the apparatus in order to enter into another in case of need. U is the cathode, as above described. V the junction of the reaction vessel with the next cathode. The partitions are formed by clay cells. The sodium formed there produces with the water floating on the mercury a caustic liquor, which through V travels to the reaction-vessels of the next cathode series U', and at V' issues as a highly concentrated solution of almost chemically pure NaOH. Thus solutions with 57 per cent. NaOH can be prepared. If the reaction-vessel is made tight and no water is employed, sodium, potassium, aluminium, &c. can be obtained in the metallic state.

Later on (Germ. pat. 73224) Kellner tries to utilize the heat liberated in the secondary processes of electrolysis for reducing the energy required for the primary decomposition. For this purpose he employs the mercury coming from the cathode of a decomposing cell as anode in another cell (p. 691), making use of a third electrode for re-conveying the heat, transformed into electricity, into the decomposing cell, and thus reducing the amount of primary current in the latter. The "decomposing space" contains a suitable anode and a cathode in the shape of mercury, which at the same time serves as anode in the "formation space," and is there opposed to a third electrode. In order to avoid the loss of heat-energy by the reaction of Na on  $H_2O$ , as well as the polarization by the hydrogen formed thereby, sodium nitrate is added to the water in the formation space, and thus,

besides caustic soda, ammonia is obtained, which is easily recovered in the evaporation of the liquor.

In his English patent, No. 13722, 1893, we find the following description:—A solution of sodium chloride is pumped into a closed vessel containing horizontal rows of carbon or platinum plates serving as anodes, the cathode being formed by mercury resting on the bottom of the vessel. At the top chlorine escapes, at the bottom sodium amalgam is formed, which from the centrally depressed bottom of the vessel flows into a funnel conveying it on to the sloping floor of a second vessel, which is fed with a solution of sodium nitrate from a reservoir placed above it. The sloping floor consists of corrugated sheet-iron, covered with gilt, silvered, or platinized wire gauze serving as electrode, the amalgam forming the other electrode; the electrical energy developed by this couple is utilized by re-conducting it into the first cell. The sodium amalgam decomposes the solution of  $\text{NaNO}_3$ , with formation of  $\text{NaOH}$  and  $\text{NH}_3$ ; the mercury freed from sodium runs off at the lower end of the bottom, passes through a cooling-pipe, and is introduced by a force-pump into the decomposing-vessel near the periphery of the depressed central part, where it is conducted in a spiral course by a specially shaped channel, and during this circulation again takes up sodium. It is an important condition that the surface of the carbon anodes must be greater than that of the mercury cathode.

Patent No. 24274, 1893, furnishes yet another apparatus. Here the bottom of a vessel, glazed at the sides and porous, dips into the electrolyte; the porous bottom is covered by a thin layer of mercury serving as cathode. The anodes are either placed on the sides or at the bottom of the vessel; in the latter case deflecting plates prevent the gas given off there from getting at the porous bottom. Thus the mercury is protected from direct contact with the electrolyte, and loss is prevented.

Again an entirely new apparatus is shown by Kellner's German patent No. 80212, and in his English patents No. 7458, 1895, and No. 20259, 1895.

According to *Zschr. f. Elektrotechn. und Elektrochemie*, 1894, p. 431, there existed a small experimental works at Hallein for producing caustic soda and chlorine by Kellner's process; a large plant was to be erected there which was to start with utilizing 2500 H.P. of the Salzach river (end of 1894). A further water-

power, amounting to 5000 H.P., was to be made available for the same purpose at Borregaard (Sarpsborg), in Norway. Unfortunately it is not stated which of the numerous processes of Kellner's was to be practically introduced.

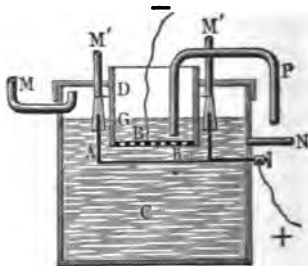
Vautin (Engl. pat. 2293, 1893) supports the mercury cathode B, fig. 217, by a wire gauze *b*, forming the bottom of chamber D;

the meshes of the gauze do not permit the mercury to pass through, but cause its immediate contact with the electrolyte, so that no diaphragm is required. A is the anode; above, the mercury vessel D is filled with water, G. The electrolyte is entirely separated from D. Since along the edges, owing to capillary depression, the layer of mercury would be too thin and the electrolyte might leak through, a strip of iron plated with sodium amalgam is attached to the inner lower edge of D, which causes adhesion with the mercury. Or else chamber D itself is made of metal, covered with an insulating layer with the exception of the lower edge. The patent describes also other shapes of cells in which a vertical or inclined layer of mercury is employed. In all cases the sodium formed at the mercury cathode passes through it, and collects at the top as sodium amalgam, or else, if covered there with water, it is changed into caustic soda, entirely separated from the electrolyte. [Vautin himself says, in Journ. Soc. Chem. Ind. 1894, p. 448: "this method worked fairly well"; but he there describes *another* method in which fused sodium chloride was employed. This probably means that the process was not found practicable.]

Drake's patent (No. 7985, 1894) gives nothing new of any importance.

J. C. Richardson (No. 22613, 1894) makes the mercury circulate in a special chamber, where it is connected by a conductor with a second cathode, in presence of the solvent intended for the cation. The second cathode is in contact with  $\text{CuO}$ , which oxidizes the hydrogen. Thus the cation is better dissolved, the mercury acts in a regular way as conveyor of the cation, and since the finally separated element is not hydrogen, but copper, there is

Fig. 217.





no gas resistance or polarization, and thus there is a saving of electrical energy.

Hulin (Germ. pat. 80398) transforms electrolytically obtained alloys of alkaline metals into alkali, by introducing them into a closed vessel filled with hydrogen, in the upper part of which a dish of water and an opening closed by a tap is arranged. By gentle heating the alloy is melted, a little water is evaporated from the dish, and the steam then forms a slight quantity of alkali on the top of the alloy. This alkali acts upon the alloy below so that the water of hydration with the alkaline metal first forms an oxide, the hydrogen escaping through the melted caustic alkali and causing a good mixture. Thus gradually the whole of the alkaline metal is quickly oxidized by the mediation of caustic alkali without any direct action of the water or the steam upon the alloy, and without any oxidation of the heavy metal. [This process is evidently in the first place intended to apply to an alloy of lead and sodium, obtained according to the inventor's patent No. 79435, to be mentioned below, but it applies also to sodium amalgam.]

Stoermer (Engl. pat. 10445, 1895) keeps the mercury cathode in a state of constant oscillation, but not sufficient to break the film of the mercury, to prevent the alkaline metal from taking up oxygen and being lost. When charged with amalgam, the cathode metal is run off and the alkaline metal separated.

Rosenbaum (Engl. pat. 17288, 1895) employs circular cells, sealed at the bottom by a revolving tray containing mercury, which first receives the alkaline metal produced by the electrolysis of alkaline chlorides, and at another place allows that metal to be oxidized by electrolytically produced oxygen.

## CHAPTER XXVII.

## IV. ELECTROLYSIS OF CHLORIDES IN THE STATE OF FUSION.

THE electrolysis of fused chlorides of the alkalis and alkaline earths is one of the oldest applications of the electric current; in this way Davy, Bunsen, and others first prepared the alkaline and earthy-alkaline metals. The technical methods worked out for this object interest us only so far as the alkaline metals are intended to be transformed into caustic alkalis by decomposing water, either immediately on their formation or directly afterwards. This has been the aim of many inventors who desire to avoid the loss of current by secondary conduction and electrolysis of the products of electrolysis (p. 634), as well as the chemical reaction between these products (p. 633). Theoretically the electromotive force required for decomposing fused chlorides is much greater than for decomposing the corresponding aqueous solutions, because the heat of formation belonging to the secondary reaction (*e. g.*  $\text{Na} + \text{H}_2\text{O} = \text{NaOH} + \text{H}$ ) in the latter case reduces the electromotive force required for splitting up the molecule. This heat of formation of course appears also during the reaction of sodium with water, if carried on *after* the electrolysis of  $\text{NaCl}$  into  $\text{Na}$  and  $\text{Cl}$  outside the cell, but in this case it is only manifested as tangible heat which can but rarely be utilized. The decomposition of the alkaline chlorides in the fused state ought therefore to require much more current tension, and therefore to consume more work in the dynamo than the decomposition in the state of solution, if the calculation were made on the basis of the heats of formation, as explained p. 636. Practically, however, the E.M.F., during the electrolysis of fused chlorides is much *below* that calculated as above. This is evidently to be explained by the fact that these methods can be carried out only at very high

temperatures, viz. above the fusing-point of the chlorides, and that the heat, brought in from without in heating the baths to that temperature, supplies part of the energy.

Thus, for instance, the E.M.F., in preparing sodium by the electrolysis of caustic soda, according to Castner's method, is said to amount to only 1 volt.

In the following pages we shall enumerate only those processes which treat of the electrolytic production of alkaline metals from their *chlorides*, essentially for the object of transforming the Na into NaOH. We therefore do not take notice of the processes for producing the alkaline metal as such in a commercial form, among which that of Castner (Engl. pat. 13356, 1890) has had the greatest practical success. Castner does not electrolyze NaCl, but NaOH; his process, which requires a tension of 1 volt, is stated to work admirably at Oldbury. Others employ for this purpose sodium chloride, as Grabau (Germ. pat. 56280) and Borchers (Zschr. f. angew. Chem. 1893, p. 487).

Werdermann (Engl. pat. 1933 & 1934, 1873) believed that by the electrolysis of fused sodium chloride with carbon anodes he had produced "sodium subchloride," Na<sub>2</sub>Cl (*sic*), and was able to decompose this subsequently by water into caustic soda and sodium chloride:



Grabau (Engl. pat. 15792, 1889) produces sodium as follows:— It has been found that earthenware vessels soon become useless, but not in consequence of the heat, but owing to the passage of the electric current. To obviate this the porcelain cell is made with a double wall, the top of which rises above the level of the molten chloride, so as to leave a clear gap between this and the molten metal; the current then does not pass through the earthenware, but round underneath into the metal contained in the bell-shaped cell, the metal rising into this cell on account of its lower specific gravity. A delivery-pipe leads away from the top of the cell to a receiver containing petroleum in an atmosphere of nitrogen or hydrogen.

According to his patent No. 16060, 1890, the formation of sodium subchloride is avoided by mixing 1 mol. KCl with 1 mol. NaCl, and adding to each 3 molecules of the mixed chlorides 1 mol. strontium chloride (which is better than calcium chloride).

This mixture melts at a temperature much below red heat, so that no subchloride is formed. The sodium produced contains 3 per cent. potassium, but no strontium.

Burghardt (Engl. pat. 12977, 1892) passes the alkaline metal produced by Grabau's method in the state of vapour through a pipe into which steam is injected at the same time, at such temperature that the caustic soda remains liquid and can be run away into iron drums to solidify.

Stoerck (Engl. pat. 15649, 1892) adds to the fused chloride some fluoride, which does not itself take part in the decomposition but promotes that of the chloride. He describes a special apparatus for electrolysis, the bottom of which is hydraulically sealed by molten lead.

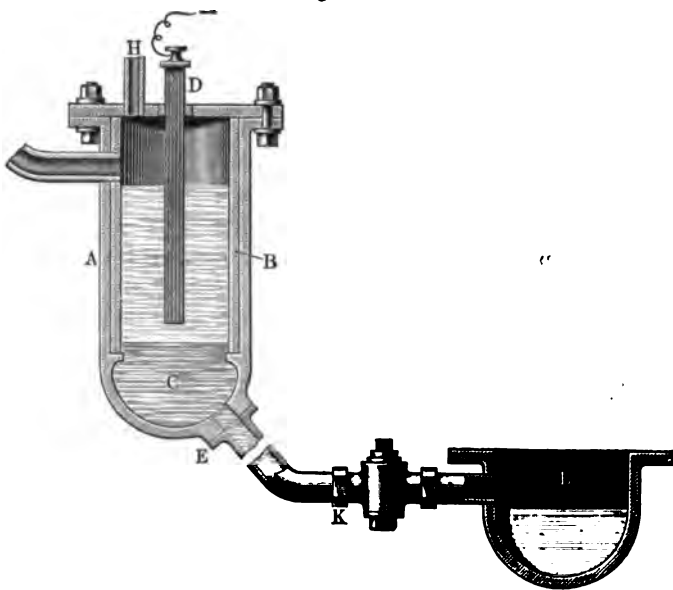
Bull (Engl. pat. 10735, 1892) melts the chloride in a covered cast-iron vessel, preferably by a regenerative gas-producer. A porcelain-lined tube dips underneath the melted chloride, and prevents the products of electrolysis from re-uniting. The electrodes consist of carbon and iron rods.

Vautin (Engl. pat. 13568 & 20404, 1893; Journ. Soc. Chem. Ind. 1894, p. 448) describes experiments on the electrolysis of molten sodium chloride, with employment of a cathode of molten lead, in which the reduced sodium dissolves as an alloy, from which it is possible to produce either sodium by distillation, or caustic soda by decomposition with water. He found, on comparing the work with molten sodium chloride and that with a solution of the same salt, under exactly similar circumstances, and with an apparatus of the same size, that in the former case the E.M.F. was 2 volts, and 4 ampères could be passed through; while in the latter case the tension was  $3\frac{1}{2}$  volts, and only 1.4 ampères passed through—demonstrating that at least 5 times the quantity of current could be passed through the fused salt as is possible through the solution at the same pressure. He proposes to employ steel crucibles of cylindrical shape, with semicircular bottom, A, fig. 218; the cylindrical part is protected by a magnesia lining, B, reaching below the surface of the molten lead. Thus the whole crucible becomes a cathode, and current can be taken away at E. From the bottom of the crucible a tap with pipe K leads to the caustic pot L. When the lead in A has taken up enough sodium, the liquid alloy is run through K into L, and is there transformed by steam &c. into caustic soda and lead; then molten lead is again

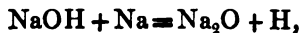
run into A, and so on. The iron cover of A is protected against the action of chlorine by dipping it into fused salt, which on solidifying coats it with a crust, and does not fuse again during the process. [This is extremely doubtful!] Cast-iron is not suitable for the decomposing crucible, because the salt would sweat through; if lined with magnesia, it would do better; but steel is preferable. The heating may be produced by the electric current itself from within, which causes much less wear and tear than heating from without.

The lead is allowed to absorb from 10 to 20 per cent. Na, and

Fig. 218.



is then treated by one of the following methods:—The alloy is broken up and put into water, whereby caustic soda is formed at once; or else it is melted in an iron pot and exposed to the action of steam, thus producing fused caustic soda, which is ladled off from the lead; or else this is done by a continuous process (comp. Hulin, p. 699). The sodium-lead alloy may also be converted into sodium oxide by melting with caustic soda,



and the  $\text{Na}_2\text{O}$  may then serve for producing sodium peroxide; it

may also be employed for the manufacture of cyanide, by fusion with potassium ferrocyanide, or of metallic sodium, by distillation. The E.M.F. required is a little below 2 volts. The anodes are made of retort-carbon, boiled with a concentrated solution of sugar and again carefully carbonized. They then stand for months without any visible wear and tear, and are not, like ordinary gas-carbon, converted by the chlorine into a mass offering strong electrical resistance.

In *Zschr. f. Elektrotechn. u. Elektrochem.* 1894, p. 250, it is stated that the electrolysis of molten alkaline chlorides with cathodes consisting of molten lead had been patented by Napier as early as 1844 (No. 10362 & 10684). But these patents do not treat of the electrolysis of alkaline chlorides, but of those of copper ores, and cannot be considered to interfere with Vautin's process.

According to the 31st Alkali Report (for 1894) the Vautin process had been tried for a short time on a small manufacturing scale at Kearsley, but it had been again suspended.

According to a further patent of Vautin's (No. 10197, 1894), free alkaline metals are to be obtained by distillation from the lead alloy.

Hulin (Germ. pat. 79435) decomposes fused alkaline chlorides, employing several anodes (?), one set consisting of carbon, the other of a heavy metal or an oxide of that metal and coal, in order to obtain an alloy of the alkaline metal with the heavy metal.

#### *Electrolysis of Lead Chloride.*

Already in 1869, Crockford (No. 3204) patented the electrolysis of lead chloride to produce chlorine and lead, but this could not at that time lead to any practical result. This process has become of importance recently through F. M. Lyte. He employs the following apparatus (pat. No. 7594, 1893):—A cast-iron pot, A, fig. 219, heated by a fire MN above the melting-point of lead chloride (and lead), contains a decomposing-bell B, consisting of stoneware or other resisting material, and dipping with its lower edge into the molten lead L. The bell is partially filled with lead chloride C; in its upper part the chlorine collects. The pressure of the liquid  $PbCl_2$ , C causes the level of the lead outside the cell to be higher than within; the excess of lead, which is

constantly forming, is removed by the overflow D. E are the carbon anodes, passing through the cover of B, and reaching downwards in C almost to the level of the lead L, forming the cathode. F is a pipe serving for charging fresh lead chloride, sealed at the bottom by the molten lead chloride. The iron cover A' holds the

Fig. 219.

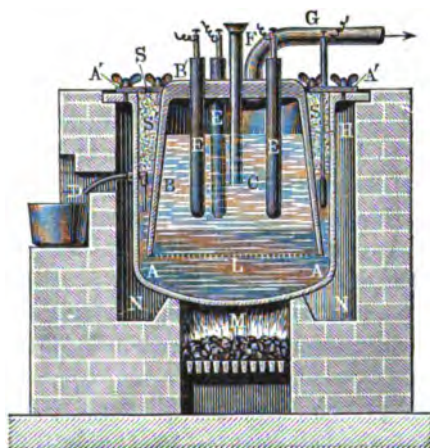
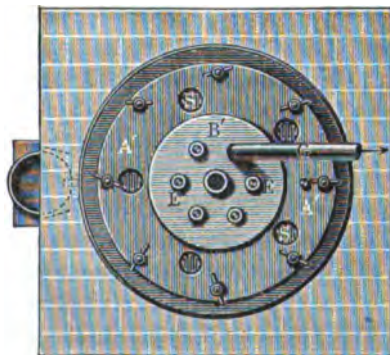


Fig. 220.



bell B within vessel A ; B fits exactly into an opening of A', and all round there are small holes S, in order to fill the space S' about the upper portion of the bell with ground coal, sand, &c. These materials float on the lead outside the bell and prevent its oxidation and the radiation of heat. Since the bell A has to

sustain only the pressure corresponding to the upper portion of the molten chloride, it need not have very thick walls, and it may consist of any material refractory to heat and chlorine, as stoneware or plumbago. The joints between the cover of the cell and the anodes and pipes are made air-tight by a cement of asbestos and silicate of soda. If B is made of plumbago or other conducting material, the anodes must be carried through insulated. Since the pot A is not exposed to the influence of chlorine, it may be made of cast-iron; the electrical connection is then either made by a tinned iron rod H dipping into the lead forming the cathode, or by the vessel A itself being tinned inside to produce good contact with the lead. The overflow pipe D bends a little down inside to prevent obstruction by the sand. The anodes E are tubular carbons, closed at the ends and rounded off outside. They contain a metal core, or a fusible metal or alloy whose melting-point is below that of lead; into this core a rod projects from the pole in such a manner that a good electrical contact is made without mechanically straining the carbon by the expansion of the metal in heating.

In working the process, first A is filled up with molten lead to a sufficient height, the bell B is put in, and lead chloride is introduced through F in the state of powder or fused, until the outer level of the lead has reached the normal height; ground coal or sand is put in through S. As the liquid lead runs off through D, more lead chloride is fed through F, so as to keep the level as equal as possible. (The cathode described is protected by a special patent, comp. Chap. XXX.)

A further patent (No. 7264, 1893) improves the process by displacing the air contained in the apparatus, before commencing the electrolysis, by chlorine or nitrogen, in order to prevent the injurious action of oxygen on the anode carbon.

In carrying out this process, we must remember that the fusing-point of lead chloride is about  $500^{\circ}\text{C}$ . (various authors state it between  $485^{\circ}$  and  $510^{\circ}$ ); its boiling-point, according to Carnelley and Williams (*Journ. Chem. Soc.* xxxvii. p. 126), is between  $861^{\circ}$  and  $954^{\circ}\text{C}$ . Metallic lead melts at  $326^{\circ}$  and boils between  $1090^{\circ}$  and  $1450^{\circ}$ . The specific gravity of lead chloride is 5.8 (metallic lead 11.3); in the fused state it is an excellent conductor for electricity, viz. at  $510^{\circ}$ ,  $22500 \cdot 10^{-7}$ ; at  $580^{\circ}$ ,  $30000 \cdot 10^{-7}$ , expressed in units of mercury. Its decomposing-tension has been



found by Lorenz (Zeitsch. f. Elektrochemie, ii. p. 333) to vary between 1.1 and 0.1 volt, according to the intensity of the current.

The lead chloride necessary for Lyte's process can be procured in various ways (patents Nos. 4068, 5352, 8692, 17745, 21464, of 1891 ; 7264, 13654, 13655, of 1893, the last taken in conjunction with G. Lunge). Lead sulphate may be decomposed by a strong solution of magnesium and sodium chloride; most of the  $PbCl_2$  crystallizes from the solution on cooling. The silver present is precipitated by zinc; the alkaline sulphate is separated by further cooling, and at last the remainder of the lead by a fresh addition of alkaline chlorides, &c. Or lead oxide is converted into chloride by means of hydrochloric acid or ammonium chloride. Lead nitrate is decomposed with calcium or magnesium chloride into lead chloride and the nitrates of calcium or magnesium, from which the nitric acid is recovered by heating. Or  $PbCl_2$  is made from  $PbO$  or lead nitrate by  $HCl$ ; in the last case free nitric acid is formed. In all cases the lead nitrate is first treated with finely divided lead, in order to precipitate the silver present in the crude lead.

Special attention is paid to the combination of the process with the utilization of the chlorine from the *calcium and magnesium chloride*, contained, *e. g.*, in the waste liquor from the *ammonia-soda* and the *potassium-chloride* manufacture. These are decomposed by lead nitrate into lead chloride and the nitrate of the alkaline earth; by heating the latter, the alkaline earth and the nitric acid are split off and are separately recovered. Magnesium chloride may also be obtained from  $CaCl_2$  by means of the Schaffner-Helbig process (treatment with  $MgO$  and  $CO_2$ ). The calcium nitrate, after separating the crystallized  $PbCl_2$ , still holds some of it in solution; this can be almost completely precipitated by slightly acidulating with hydrochloric or nitric acid; the slight proportion of chlorine produced in the former case has a favourable action when employing the recovered nitric acid for dissolving lead oxide by precipitating the silver. The  $PbCl_2$  may also be precipitated by lime, &c. as oxychloride, or by calcium sulphide as lead sulphide. Calcium or magnesium nitrate is decomposed at a low red heat; the vapours are treated with air and water for the recovery of nitric acid. Any undecomposed nitrate is washed out of the residue by water. The recovered nitric acid is employed

for dissolving lead oxide (massicot); this is obtained either by oxidizing the metallic lead obtained in the electrolysis of the chloride or from commercial lead. In the latter case the solution contains silver, and is *desilverized* by the addition of spongy lead before adding the calcium chloride. The  $\text{PbCl}_2$  is then precipitated, washed, dried, and electrolyzed as above described.

The principal process for obtaining the lead chloride is that which is described in the later patents, partly together with Lunge. Sodium nitrate is treated with ferric oxide, and from the residue caustic soda and ferric oxide (partially in the shape of Venetian red) are recovered. The vapours are condensed to nitric acid, and lead oxide is dissolved in the latter. The lead nitrate is decomposed by sodium chloride into lead chloride and sodium nitrate; most of the  $\text{PbCl}_2$  crystallizes out on cooling; the remainder is precipitated by lime, soda, or lead oxide as basic lead chloride. The lead chloride is electrolyzed as described, p. 704, and furnishes chlorine and metallic lead, which is oxidized to  $\text{PbO}$ , and is then dissolved in the nitric acid recovered from the sodium nitrate by igniting with ferric oxide.

## CHAPTER XXVIII.

## CHLORINE FROM HYDROCHLORIC ACID: BLEACH-LIQUOR.

V. ELECTROLYTIC PRODUCTION OF CHLORINE FROM  
HYDROCHLORIC ACID AND *vice versâ*.

GEISENBERGER (prov. prot. No. 8104, 1883) produces a current by the action of hydrochloric acid on plates of zinc and carbon, arranged in couples, and by means of this current he decomposes the zinc chloride, generated in the first vessel, in a second vessel into chlorine and metallic zinc.

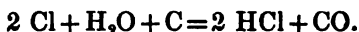
Höpfner (Engl. pat. 19375, 1891) makes chlorine from hydrochloric acid, or from a mixture of a chloride with sulphuric acid. The solution circulates in the electrolytic apparatus, and is always brought back again to the same strength by adding aqueous hydrochloric acid or blowing in gaseous HCl. This process is specially adapted for the recovery of chlorine from the calcium-chloride liquors of the Weldon and the ammonia-soda process, which are decomposed by sulphuric acid and then electrolyzed. The diaphragms are made by nitro-parchment, which is not acted upon by chlorine, but does not resist reduction at the cathode in the presence of alkali; therefore a second parchment-paper, non-nitrated, is employed next to the cathode.

Kellner (Engl. pat. 20060, 1891) makes chlorine from hot hydrochloric acid, together with hydrogen, in acid-proof apparatus, consisting of superposed tanks, divided by ribs into longitudinal cells and containing horizontal electrodes. The hydrochloric acid is made to flow through all the compartments from top to bottom, and is heated by indirect steam. [This procedure is technically impossible; the lead worm would be dissolved in a very short time by hot hydrochloric acid.]

Oettel (Zschr. f. Elektrochemie, 1895, p. 57) has made laboratory experiments on the electrolysis of hydrochloric acid. He shows that the highest yield of chlorine is attained by increasing the current-density at the cathode, and thereby diminishing the reducing action of hydrogen; further by diminishing the solubility of chlorine in the acid through the addition of various salts. In the latter case the yield of chlorine may go up to 92 to 98 per cent. of the theoretical.

Knorre (Germ. pat. No. 83565) proceeds upon the last-mentioned principle by dissolving about 160 grams NaCl in 1 litre 7 per cent. hydrochloric acid, previous to electrolyzing. The HCl can thus be entirely decomposed, the yield being at first 98 per cent., and ultimately 85 per cent. of the theoretical. When only traces of free HCl are left, the solution of NaCl is re-employed for absorbing HCl in the ordinary manufacturing process. The electrodes are made of carbon; no diaphragms are required. The process is founded upon the intermediary formation of sodium hypochlorite and its subsequent decomposition by hydrochloric acid, which takes place even in the most dilute solutions.

*The conversion of free electrolytic chlorine into hydrochloric acid* is a problem which till now would have appeared to possess exclusively theoretical interest. The development of electrolytic methods may, however, lead to such changes in the respective values of free chlorine and hydrochloric acid, that the manufacture of the latter from the former, hitherto a technical absurdity, might become a reality. No doubt means would then be found for combining Cl and H without incurring the danger of explosion. In this connection it is also interesting to note that Lorenz (Zeitsch. f. anorgan. Chem. x. p. 74) has shown that a mixture of chlorine and steam, when passed through a porcelain tube filled with charcoal and heated to a dark red heat, is immediately and quantitatively converted into a mixture of HCl and CO:



When washing out the HCl by water, almost pure carbon monoxide is obtained, and this might be employed for heating the apparatus. This proposal has been patented by the inventor (Engl. pat. 25073, 1894).

## VI. PREPARATION OF BLEACH-LIQUORS BY ELECTROLYSIS OF CHLORIDES.

According to Chem. Ind. 1893, p. 129, as early as 1820 Brand bleached calico electrolytically between two platinum plates. This must have been an experiment made on a small scale, coming at least sixty years before the time when such a process could have the slightest prospect of realization for industrial purposes.

Hermite was one of the first to develop electrolytic bleaching by means of chlorine obtained from calcium or magnesium chloride. His first English patents are Nos. 5160, 1883, and 13929, 1884. The best results are said to be obtained with solution of magnesium chloride of spec. grav. 1.125, or calcium chloride spec. grav. 1.190; these solutions are always regenerated by the bleaching process. The cathodes consist of zinc, the anodes of platinum. Only a ninth part of the chlorine is required of that which is consumed in ordinary bleaching. The chemical equations which are to explain this are of a more than doubtful kind and are not worth repeating. Patent No. 3957, 1886 (p. 686), in which a mercury cathode is employed, does not seem to have been carried out on a large scale. In patents Nos. 14673, 1886, and 1993, 1887, Hermite, Paterson, and Cooper describe a tank with perforated partition, with electrodes of zinc and platinum and a screw propeller, which keeps the liquid in constant circulation and impels it towards the electrodes. The zinc is constantly scraped by mechanically moved knives, in order to prevent any deposits accumulating thereon.

A further patent by Hermite, Paterson, and Cooper (Germ. pat. 49851) recommends for electrolytic bleaching a solution of 1 part magnesium chloride and 4 parts rock-salt, of spec. grav. 1.03, or a 5 or 6 per cent. solution of carnallite, to which a little magnesia is added in order to keep the bath alkaline. Another mixture is given in Hermite's English patent No. 5393, 1887:—



Cross and Bevan (Journ. Soc. Chem. Ind. 1887, p. 170) made an extremely favourable report on the Hermite process in which they asserted that the bleaching-action of the electrolyzed solution of magnesium chloride (which is the one practically employed) is

greater than that of a solution of chloride of lime (bleaching-powder) of equal oxidizing power with reference to arsenious acid, in the proportion of 5 : 3 ; also that the oxidizing action (the formation of free oxygen) is superior to that which is calculated from Faraday's law. [The former is probably simply explained by the fact that magnesium hydrochlorite, prepared in a certain way, is less stable than calcium hypochlorite and has a quicker bleaching-action (p. 497) ; the latter may have been caused by uncertainties in measuring, the more so as the difference is but slight.] The best concentration of the solution of  $\text{MgCl}_2$ , they found to be  $2\frac{1}{2}$  per cent. The cost of the process is calculated as follows:—The minimal yield of available chlorine was found = 1.25 grams per ampère-hour, at a tension of 5 volts, and the estimate is 570 H.P. per hour for 2 cwt. chlorine = 6 cwt. bleaching-powder. Since they assume the bleaching-efficiency of this chlorine to be as 5 : 3 of that of ordinary bleaching-powder, 570 H.P. would be the equivalent of 10 cwt. of bleaching-powder per hour, or 50 H.P. that of a ton of bleaching-powder in 24 hours. Taking the cost of a H.P. as £9 per year of 300 working days, we arrive at £1 10s. as the equivalent of a ton of bleaching-powder, for electricity produced by steam. To this they add £1 for interest and depreciation, altogether £2 10s. [which does not allow for any other expenses].

Cross and Bevan's paper was strongly attacked by Armstrong (Journ. Soc. Chem. Ind. 1887, p. 246) and especially by Hurter (*ibidem*, p. 337) ; the latter, on the basis of his own experiments and analyses, declared their results to be erroneous and entirely impossible. According to his calculation, the electrolytic equivalent of a ton of bleaching-powder would be, not £2 10s., but from £22 to £42.

Cross and Bevan (*ibid.* 1888, p. 292) replied to this criticism by a long series of laboratory and bleaching experiments on a larger scale, contrasting strongly with Hurter's assertions and results. Hurter's reply (*ibid.* p. 726) explained a few smaller contradictions, but on the whole these discussions did not throw any light upon their enormous discrepancy in the valuation of the Hermite process which, according to reports from America, was at that time in full profitable operation at a paper-mill. On the other hand, the English paper-mill where those first excellent results had been obtained abandoned the

process and sold the apparatus as old iron. But the process made its way again in other places, as is proved by the following notes, from which it appears that it is not at present applied to magnesium chloride but to sodium chloride.

According to the 'Papier-Zeitung,' 1894, p. 427, the Hermite process is in operation at the sulphate-cellulose works at Stjernfors near Uddeholm (Sweden). During the last four years they had bleached 35 cwt. every day, with water-power amounting to 75 H.P., and a decomposition of 110 kil. salt per ton of cellulose. Although the power required is twice as high as stated by Cross and Bevan, the bleaching at that place is cheaper than by means of bleaching-powder. Cross and Bevan (Journ. Soc. Chem. Ind. 1892, p. 964) state that the Hermite process, "to prove the utter absurdity of which a considerable amount of energy was devoted by a distinguished authority, has proved itself highly successful on the Continent. At the present it is replacing 3000 tons of bleaching-powder per annum."

Fischer's Jahresb. 1889, p. 1175, contains a description of the application of this process at a Cardiff paper-mill.

The process of Hermite for *disinfecting sewage* by the electrolysis of sea-water or artificial compositions of a similar kind cannot be treated here: I only refer to the detailed report by Roscoe and Lunt (Journ. Soc. Chem. Ind. 1895, p. 224) and a number of investigations published in the Zeitsch. f. Elektrochemie, ii. (1895-96) pp. 66, 88.

Stepanow (Germ. pat. 61708) employs a solution of sodium chloride containing lime, the reaction being:



Half of the caustic soda formed is decomposed with the  $\text{CaCl}_2$  into  $\text{NaCl}$  and precipitated  $\text{CaO}_2\text{H}_2$ ; the other half remains in solution. His apparatus consists of many lead boxes, suspended in tiers from a sloping frame, the electrolyte running gradually through all of them; the boxes serve as cathodes, and the anodes consist of platinum-foil.

Kellner (Engl. pat. 10200, 1892) prepares a bleaching-liquor by combining the ions produced by electrolysis outside the apparatus. The chlorine enters at the bottom of an absorbing-tower, through which drops the alkaline liquor coming from the cathode space,

after having been liberated from the hydrogen carried along by violent agitation.

According to another patent (No. 13723, 1893) Kellner proceeds as follows:—A trough A, figs. 221, 222, 223, is closed by a cover

Fig. 221.

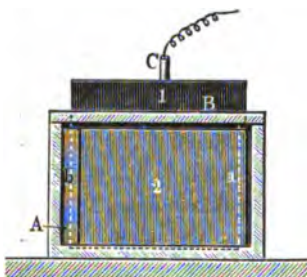


Fig. 222.

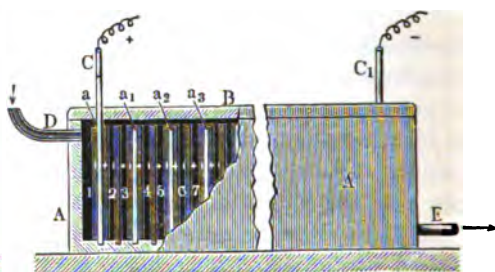
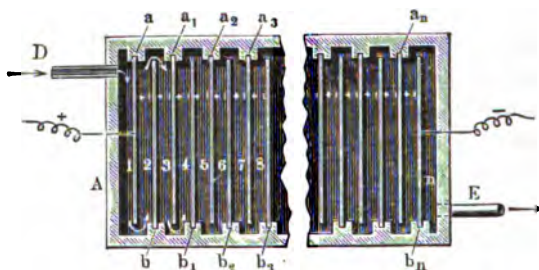


Fig. 223.



B, and is provided at two opposite sides with alternately placed grooved ledges  $a, a_1, \dots a_n, b, b_1, \dots b_n$ . In these grooves the electrodes 1, 2, 3  $\dots n$ , consisting of carbon or of metal platinized on one side [this would not do, as no platinizing will protect the underlying metal for any length of time!], are placed in such manner that their free ends reach into the space lying between each two opposite ledges. The first and the last electrode project from trough A through cover B and bear the contacts C and  $C_1$ . The solution of sodium chloride is introduced by pipe D into A and runs off through E, after having travelled in a zigzag course between the electrodes in the direction of the arrows. The electrodes divide the whole space into a row of cells, and act always on one side as anodes, on the other as cathodes. In consequence



of the electrolyte having to pass between the electrodes and the ledges  $a$  to  $a_n$  and  $b$  to  $b_n$ , any loss of current is avoided, and every cell behaves like a separate element. If, *e. g.*, a dynamo of 99 volts and 32 amps. is at disposal, 23 electrode-plates will be employed, forming together 22 cells; in each cell there is a tension of 4.5 volts and a current of 32 amps. will pass; thus the action of a current of 4.5 volts and 704 amps. will be attained. From the NaCl solution chlorine is evolved at all anodes, and NaOH is formed at all cathodes; the liquid travelling through the apparatus brings them both together, and combines them into sodium hypochlorite; the hydrogen disengaged on the cathode side is harmless owing to the quickness of the flow. The bleaching-liquor issuing from E is carried into the vessel where the bleaching has to take place, and from this returns into the decomposing-vessel. If carbon-plates are employed as electrodes, a filter is interposed between trough A and the bleaching-vessel, consisting of glass-wool contained between two perforated plates or metallic tissues.

A further patent of Kellner's (No. 19542, 1893) describes "bleaching-blocks," to be lowered into beating-engines for paper-pulp, consisting of insulated plates of copper, gun-metal, or phosphorous bronze, covered on the anode side with platinum-foil and amalgamated on the cathode side. The beating-engine is filled with a solution of sodium chloride, which on closing the circuit is changed into a bleaching-solution. Another form of this is described in No. 8206, 1894.

A German patent of Kellner's (no. 69780) prescribes increasing the energy of free chlorine by the dark current between electrodes.

Montgomery (Engl. pat. 2329, 1892) proposes to promote electrolytical bleaching by driving a current of air through the bath, which is supposed to promote oxidation and at the same time to bring the products of electrolysis into intimate contact with the textile fabrics.

Andreoli (Germ. pat. 51534) prepares a bleaching-liquor from NaCl solution of spec. grav. 1.089; there is always one cathode between two anodes of much greater surface. For the oxidation of hydrogen the cathodes are surrounded by wire gauze filled with small pieces of manganese ore. An English patent of the same inventor's (No. 8161, 1888) described anodes cast from lead chloride, and subsequently by reduction and oxidation transformed into lead peroxide, in combination with manganous chloride; also

several varieties of electrodes, including the application of alternate currents and heating the bath to 60° C. Again, quite different from this is a report on Andreoli's process (which seems to have undergone many changes) in Fischer's *Jahresb.* 1890, p. 1111.

Andreoli (Engl. pat. 1661, 1893) further describes an apparatus for electrolyzing not merely chlorides, but also sulphates and nitrates. The cell is a trough of iron, within which stands a trough made of carbon or of several layers of wire gauze, electrically connected with the former (auxiliary cathode); in the latter the carbon or platinum anodes are suspended. Inside the anode compartment sodium hypochlorite is formed, outside caustic soda and hydrogen. The auxiliary cathodes are to reduce the electrical resistance. In this way a row of cells can be formed through which the liquids flow from both chambers, one after the other, and thereby are concentrated; the hypochlorite solution from the anode chamber is cooled, to avoid the formation of chlorate.

Knöfler and Gebauer (Engl. pat. 20214, 1892) describe the following apparatus as being especially adapted for producing bleaching-solutions by means of currents of high tension. The electrodes are thin plates, separated by insulating frames, kept together as in a filter-press, with india-rubber or asbestos washers—each electrode acting on one side as an anode, on the other as a cathode. They may consist of platinum, carbon, manganese peroxide, lead peroxide, &c. With platinum, sheets of 1 mill. thickness may be used and 10 or more ampères may be passed through per gram platinum, employed as a sheet with a surface of 100 square centimetres. Since, except at the end plates, no contacts are necessary, the repairs are slight. Where diaphragms are necessary, they are enclosed between the frames, just like the electrodes.

In pat. No. 5578, 1893, Knöfler and Gebauer state that they electrolyze mineral salts without diaphragms with currents of 300 to 800 ampères per square metre of electrode surface, the strength of liquor in available chlorine being regulated by the temperature. When employing a 10-per-cent. solution of salt, it is possible, by feeding the apparatus with a definite quantity of solution within a given time, to keep both the temperature and the percentage of available chlorine constant without any chemical analysis. In consequence of their arrangement, by which the cells are formed by plates, serving on one side as anodes, on the other side as

cathodes [which is also the case in Kellner's apparatus, p. 714], very many cells can be worked in series. This is especially useful with platinum electrodes, which may in this case be taken as thin as 0.01 millim., and yet are fit to transmit per square decimetre surface 10 and more amps.

Hermite, Paterson, and Cooper (Engl. pat. 10930, 1895) describe a battery for converting sea-water or other saline chloride solutions into disinfectants. The battery consists of a series of glass or other suitable tubes. Within each tube is a cylinder of zinc and a platinized copper wire, which are connected alternately. The tubes are fitted with stoppers, through which narrower tubes pass, conveying the solution to be electrolyzed alternately from the bottom to the top of another tube. The solution finally runs into a reservoir, in which a float, attached to a rod travelling in guides, actuates a simple system of levers, which in turn automatically regulate the electric current and the supply of saline solution. A somewhat different form of anode is described in their patent No. 10929, 1895.

Schoop (Zsch. f. Elektrochemie, 1895, ii. pp. 209 & 227) describes experiments on the electrolysis of calcium-chloride solutions.

Oettel (Zsch. f. Elektrot. u. Elektroch. i. p. 354) and Lambert (Bull. Soc. Chem. (3) xi. p. 56) prove that liquors containing a large proportion of bleaching-chlorine cannot be obtained by electrolysis. [This would show that commercial bleach-liquor cannot be obtained in this way, but it does not interfere with the direct employment of electrolytic bleaching of fibres or paper-pulp.] Oettel's researches will be mentioned in detail when treating of the electrolytic formation of chlorates.

Engelhardt (Chem. Zeit. Repert. 1895, p. 411) asserts that electrolytical bleach-liquors can be obtained, testing 1 per cent. available chlorine, that these keep better than bleaching-powder solutions, and that the fabrics bleached with them are more easily washed free from chlorine than those bleached in the old way. He also adds the very doubtful assertion that the fabrics are less acted upon by this bleach than in the ordinary way.

*Analytical Methods for Testing Electrolytic Bleaching-Solutions.*

. Norton (Chem. News, lxvi. p. 115) proposes, for the purpose of estimating available chlorine as well as chlorides ( $\text{NaOCl}$  and  $\text{NaCl}$ ), a method which I had described many years ago, and which is in fact the simplest and best, viz. titrating the available chlorine by sodium arsenite according to Penot's method, by which the  $\text{NaOCl}$  is transformed into  $\text{NaCl}$ , and subsequently titrating the total chloride in the same solution by silver nitrate, in which case the sodium arseniate formed acts extremely well as an indicator, instead of the potassium chromate otherwise employed. By subtracting the first from the second quantity, we obtain the chloride originally present as such.

The chlorate is estimated by Norton along with the other chlorine compounds by adding an excess of standard silver solution, boiling with a solution of sulphurous acid and a little nitric acid till the excess of  $\text{SO}_2$  is expelled and all chlorine compounds are reduced to chloride, and titrating the excess of silver by means of Volhard's sulphocyanide method, employing iron-alum as indicator. From this total chlorine the previously estimated chloride and hypochlorite are deducted, in order to find the chlorate\*.

For estimating, in electrolyzed solutions of sodium chloride, free alkali in the presence of  $\text{NaOCl}$  and  $\text{NaClO}_2$ , Ullmann (Chem. Zeit. 1893, p. 1208) employs a titrated solution of succinic acid, which expels  $\text{CO}_2$  and  $\text{HOCl}$ , but not  $\text{HCl}$ , and which is stable towards oxidizing and chlorinating agents. The solution is heated with an excess of succinic acid until the smell of  $\text{HOCl}$  has vanished; then phenolphthalein is added, and the titration finished by standard soda solution.

\* I will here mention the direct estimation of chlorate, worked out by Fresenius (Zsch. f. anorgan. Chem. 1895, p. 501), and applying also to the analysis of bleaching-powder, p. 439. Acetate of lead is added to the solution till all the hypochlorite has been destroyed,  $\text{PbO}_2$  being formed. To the filtrate a slight excess of sodium carbonate is added; the solution filtered from the precipitate contains all the chlorate, which is estimated by distilling with hydrochloric acid into a solution of potassium iodide.

## CHAPTER XXIX.

## CHLORATES.

THE formation of potassium chlorate (and perchlorate) in the electrolysis of potassium chloride was observed by Kolbe many years ago, at a time when nobody thought of a technical application of electrolysis in chemical manufacture. When this was realized, inventors soon found that chlorates were unexpectedly formed, when trying to decompose the alkaline chlorides into chlorine and caustic alkali. Already in one of the first of the patents treating of electrolysis, that of Charles Watt (p. 655), this is mentioned. The real manufacture of potassium chlorate by electrolysis was first brought about by Gall and Montlaurs' patents.

Their English patent (No. 4686, 1887) gives a very brief outline of the process. The alkaline chlorides are to be electrolyzed at 50° C. in a trough, divided into two parts by a porous partition. The liquid circulates from the negative to the positive pole, so that the alkali set free at the cathode at once combines with the chlorine formed at the anode.

During a visit which I made in 1889 to the experimental works at Villers-sur-Hermès, the inventors gave me the following notes respecting the process:—The reaction is carried out in vessels, provided with diaphragms of a special construction, at such temperatures that the initially formed hypochlorite cannot exist. The concentration of the liquor is so great that the chlorate crystallizes in the bath and is fished out with ladles made of enamelled cast-iron. The current employed was 1000 amps. and 25 volts, in five baths put in series at 5 volts each, while theory requires 4.36 volts, according to Gall. In practice, 1 kil. potassium requires 1 H.P. during 24 hours. [This is 45 per cent. of the theoretical yield ;

an I.H.P. ought to yield at least 600 watts, or, with a tension of 5 volts, 120 ampères;  $120 \times 0.018305 = 2.205$  kil. would be the theoretical yield of  $\text{KClO}_3$ .]

This process was carried out in 1891 by the Société d'Electrochimie at Vallorbes in Switzerland, by means of a waterfall on the Orbe (Sant-du-Day) of 100 feet height, equal to 3000 H.P. The following details respecting the works are compiled from 'Engineering and Mining News,' 1894, p. 615, 'Revue de Chimie industrielle,' 1893, p. 89, and Monit. scient. 1894, p. 502.

Of the 3000 H.P. available, the older plant utilized about 1500, by 10 turbines of 160 H.P. each (9 for work, 1 as reserve). Later on, two new turbines at 700 H.P. each were erected. The turbines are on Jacob Riether's system, 1 metre diameter; the new, more powerful turbines are no larger, but turn more quickly than the old ones. These make 350 revolutions per minute, and are directly coupled with Thury dynamos, fitted with 6 poles, weighing 6 tons, developing 100,000 watts, and working at 150 volts. The engine possesses no governor; its regulation is brought about by the baths themselves. The current is conducted by large cables and divided in a special way. In one half of the baths the positive poles are connected with the negative poles of the other half. The point common to both groups is connected with a cable, insulated in the ground and terminating with a strip of copper, connected with the 10 machines by 10 conductors, half of which go to the positive poles of 5 dynamos, and the other half to the negative poles of the other 5 dynamos. Owing to this arrangement, each series of baths can be put out of turn by stopping the corresponding dynamo.

There are 270 baths of rectangular shape, containing about 50 cubic metres liquid. They are insulated from the floor by porcelain cups filled with oil, so that the men can touch the baths. Diaphragms insulate the anodes from the cathodes, both of which are placed at the bottom of the baths. The anodes consist of very thin sheets (0.1 millim. thick) of an alloy of 90 platinum and 10 iridium, which keeps perfectly well, whereas platinized silver wears out quickly and carbon is quite useless. The cathodes are made of iron; nickel would be preferable. The floor of the shed consists of wood, resting on porcelain cups, like the baths themselves.

The plant for water-power cost 260,000 francs, or 86 francs per H.P.; the total cost, including dynamos and buildings, was below

600,000 frs., or less than 200 frs. per H.P. The electrical part alone cost about 100 frs. per E.H.P.

The potassium chloride is employed as a 25-per-cent. solution. The tension in each bath is 5 volts; the current-density 50 amps. per square decimetre. The solution of KCl is supplied at the same time to all the baths; the mixture of the caustic liquor formed at the cathodes with the chlorine given off at the anodes is effected by continuous mechanical circulation. The temperature is kept between 45° and 55°, which is produced by the current itself; thus the hypochlorite is transformed into chlorate. The  $\text{KClO}_3$ , which is difficultly soluble in the liquid, crystallizes out for the most part; hence the liquor is run off every few hours, the crystals are separated and purified by recrystallizing, the filtered liquor is again saturated with fresh KCl in other vessels, and is then re-conveyed into the baths. There are no mother liquors going to waste; even the same supply of water serves continuously as vehicle for the manufacture. The baths must be emptied only at long intervals for the purpose of cleaning and of changing the electrodes.

The hydrogen formed by secondary reaction (100 cubic metres per ton of chlorate) escapes in bubbles which carry along a little liquor, so that the air escaping through the ventilating-shafts produces a white incrustation of potassium chloride on the roofs.—The same Company has since erected a still larger works in Savoy, at Saint-Jean-de-Maurienne.

Gibbs and Franchot (Engl. pat. 4869, 1893) manufacture alkaline chlorates by electrolyzing the chloride in a cell provided with a copper-oxide cathode, until half of the KCl has been transformed into  $\text{KClO}_3$ . The solution is then withdrawn, cooled, and allowed to crystallize. The cathode is taken out of the cell, washed, dried, re-oxidized in a current of air at a dark red heat, and replaced in the cell. The mother liquor is brought back to the former strength by adding KCl, and again electrolyzed.

Spilker and Löwe (Germ. pat. 47592; comp. p. 680) prepare potassium chlorate, together with caustic potash, as follows:—The iron cathode trough is charged with a very dilute solution of potassium chloride; the earthenware vessel placed inside the trough, and containing the carbon anodes, is charged with a solution of KCl saturated with lime. If a solution of KCl is continuously fed into the earthenware vessel at the top, a solution containing calcium hypochlorite and chloride can be drawn off from

the bottom of the vessel by means of a siphon, while at the bottom of the cathode compartment a solution of caustic potash is continuously running off. The first liquor enters into a vessel filled with lime, where the lime dissolves in the liquor, containing  $\text{CaCl}_2$  as calcium oxychloride. This liquor is first returned to the earthenware vessel, in order to take up more hypochlorite; and this process is continued until only a slight proportion of  $\text{KCl}$  is left, sufficient for conducting the current. If the liquor passes through fast enough, no smell of chlorine is perceived. At a temperature of  $40^\circ \text{C}$ ., instead of calcium hypochlorate, calcium chlorate is formed, which, with the potassium chloride, at once decomposes to calcium chloride and potassium chlorate. When the anode solution has become sufficiently strong in chlorate, it is concentrated in order to obtain the  $\text{KClO}_3$  in a solid state; the cathode liquor is worked for caustic potash.

A new German patent of Spilker's (No. 73221) describes anodes, consisting of alternately placed carbon and lead rods, electrically connected.

According to *Zsch. f. angew. Ch.* 1894, p. 89, in the practical application of the process the voltage rose from 0.8 to 1.8 volt, and did not further increase after several months' working; hence the polarization by gas was not essential. The yield of  $\text{KClO}_3$  was at first only one third of the theoretical, viz. 0.25 gram per ampère-hour; but after 36 hours it rose to 95 per cent. of the theory and then remained stationary. The lead at the anodes was covered with white lead chloride, which gradually changed into a not very firmly adhering coat of  $\text{PbO}_2$ ; the carbon was also covered with  $\text{PbO}_2$ , which in this case adhered to it very firmly. After several months' work the carbon was found intact and only the lead was corroded. The lime-mud contained a large amount of lead oxide. Hence the tension must have been less so long as the anode was covered with  $\text{PbCl}_2$ , and it increased as the  $\text{PbCl}_2$  passed into  $\text{PbO}_2$ ; but at the same time the yield of  $\text{KClO}_3$  rose nearly to the theoretical quantity. The gas polarization is avoided at the expense of the gradually corroding lead.

The Société d'Electrochimie (Fr. pat. 242073) tries to avoid some of the difficulties and losses in the manufacture of chlorates by offering to the  $\text{HCl}$ , formed at the anode, from the first sufficient alkali for neutralization, viz., bases equivalent to 200 c. cm. standard alkali to 1 litre of solution. The chlorine is then at once absorbed,



and only a little oxygen is set free at the anode, in consequence of secondary reactions. This addition of alkali also causes a purification by the precipitation of ferric oxide, &c. In order to utilize the anode metal as much as possible, the anodes are made of the thinnest possible platinum-foil; and in order to avoid reduction of the chlorate by nascent hydrogen, the cathodes are bent round the anodes so as to take the current at both sides, and are covered with asbestos cloth, which forms channels for conducting away the hydrogen and preventing it from acting upon the chlorate.

Hurter (Engl. pat. 15396, 1893) electrolyzes KCl in a metal vessel serving as cathode, which has an inside coating consisting of a mixture of Portland cement, salt, and sand, which after washing out the salt yield a porous diaphragm. The anode is a sheet of platinum suspended in the centre of the vessel. Several vessels are superposed and are worked in series, being kept apart by insulating rings. A solution of KCl, containing caustic alkali, is run on to the bottom of the top vessel; this overflows from the surface of the liquid by a non-conducting pipe on to the bottom of the next lower vessel, and so on, in order to run off from the bottom vessel. The gas can escape by pipes from the upper part of each compartment. By means of steam heating-coils (how insulated does not appear), or by the heat produced by a high current-density, the liquid is kept at the temperature suitable for the formation of chlorate.

Jobard (French pat. 209534) produces potassium chlorate by electrolysis together with *tin*, which by-product is to cover all the expense of the process (!). A concentrated neutral solution of tin protochloride is made, with addition of sodium chloride, and this is electrolyzed in a cement trough, with plumbago anodes and cathodes made of tinned iron. On the passage of the current the tin is precipitated in a solid state; the chlorine is liberated, and is passed into an apparatus where it serves for the manufacture of potassium chlorate. The loss of tin does not exceed 10 per cent. of that contained in the protochloride. The yield of  $\text{KClO}_3$  is 25 per cent. less than theoretically obtainable from the chlorine liberated by electrolysis. [This process is not adapted for the electrolytic production of potassium chlorate, but of chlorine, as such, which might be utilized in any other way. How by this process, in which 10 per cent. of tin is lost, chlorine is produced *without expense*, is known only to the inventor.]

Cutten (Amer. pat. 480492 and 480493, of 1892) electrolyzes magnesium chloride in the presence of potassium chloride and hydrated lime or magnesia, with agitation. This mixture is placed in the anode space, and magnesium chloride into the cathode space, separated by a diaphragm. In the former potassium chlorate, in the latter magnesia is formed. Very similar to this is Parker's English patent, No. 24860, 1894.

Blumenberg (Engl. pat. 9129, 1894) closes the anode cell and connects it at the top by a pipe with the bottom of the cathode cell, so that the gas liberated at the anode forms chlorate at the cathode, which is favoured by a temperature of about  $49^{\circ}\text{C}$ . The chlorate is precipitated in a separate vessel, communicating with the cathode cell by a pipe provided with a valve; from here the mother liquor is pumped into a re-saturator, and then again goes back into the cathode cell. His German patent No. 80395 contains the important modification that the chlorine produced at the anode is not directly introduced at the cathode, but is conveyed to a gas-holder, and thence into a separate vessel, where it meets with the cathode liquor. In the anode chamber a high pressure is maintained, in the cathode chamber only the ordinary atmospheric pressure.

Gall and Montlaur (French pat. 240698) prepare *sodium* chlorate as follows:—The electrolyzed solution of sodium chloride is treated with carefully washed fuel gases, containing from 10 to 20 per cent.  $\text{CO}_2$ , until all the  $\text{NaOH}$  has been converted into  $\text{Na}_2\text{CO}_3$ . The liquor is now concentrated by evaporation till the  $\text{NaCl}$ , together with most of the  $\text{Na}_2\text{CO}_3$ , has salted out. [The mother liquor is no doubt further concentrated, in order to obtain  $\text{NaClO}_3$ .] The above mixture of salts is re-introduced into the process, after causticizing the  $\text{Na}_2\text{CO}_3$  by means of quicklime.

Häussermann and Naschold (Chem. Zeit. 1894, p. 857) describe laboratory experiments on the electrolytic preparation of potassium chlorate. They made use of a square iron vessel, serving as cathode, with a suitable cell made of Pukall's porous porcelain (comp. Chap. XXX.), in which a porcelain or carbon anode was placed. The anode space contained half a litre, the cathode space one litre. The current was supplied by a dynamo of 110 volts, the amperage being kept by resistance-coils at 5 amps. Each experiment lasted 3 hours; hence 15 ampère-hours were employed, each of which by theory ought to yield

0.75 gram KOH or 0.208 KOH. The best result was obtained when a caustic-potash solution of 30 per cent. KOH was slowly run into the anode space in such a manner that the liquid was always distinctly alkaline, and no smell of chlorine was perceptible. Since carbon anodes are strongly acted upon by chlorine in an alkaline solution, a platinum-foil of  $105 \times 100$  millimetres was employed, corresponding to a current-density of 0.024 amp. to 1 square centimetre. The tension in the bath averaged 4 volts. One ampère-hour yielded 0.5 gram  $\text{KClO}_3$  = 67 per cent. of the theory, and at the cathode 1.6 gram KOH = 80 per cent. of the theory. In 100 c. c. of the cathode liquor 2.6 grams KOH was found, and 7.8 grams unchanged KCl.

Other, less favourable experiments showed that the oxygen liberated at the anode by the electrolysis of KOH cannot directly oxidize KCl to  $\text{KClO}_3$ , and that the formation of  $\text{KClO}_3$  is exclusively due to the secondary reaction between chlorine and KOH. Owing to this, the anode liquid must always contain approximately 5 molecules KCl to 1  $\text{KClO}_3$ , apart from the slight variation caused by diffusion and the small quantities of hypochlorite decomposed by the current.

The highest yield of chlorate was hence attained when the anode liquid was constantly kept slightly alkaline by a slow feed of caustic potash; with strongly acid or strongly alkaline anode liquids the quantity of chlorate obtained per ampère-hour was less. The yield of chlorate depends but to a small extent on the current-density, the temperature, and the concentration of the electrolyte, but by increasing the temperature and concentration we obtain a considerable reduction of the tension, and consequently of the amount of energy required. It is therefore preferable to employ a concentrated solution of KCl, heated to  $80^\circ \text{C}$ . Platinum is best for the anodes, but lead, lead peroxide, &c. might be employed. Instead of a pure solution of KOH, the solutions of KOH and KCl formed in the cathode space are employed for gradually running into the anode space, replacing the actually consumed potassium chloride by a fresh supply. From the anode liquid the  $\text{KClO}_3$  can be easily obtained by evaporation and crystallization, but it must be purified from KCl, which crystallizes as well, by washing with cold water and recrystallizing. The authors do not say whether this process is cheaper than the manufacture of chlorate by the old process. At all events it is,

as they believe, only possible when using a diaphragm of small electrical resistance, not acted upon by chlorine or alkali.

Oettel (Zsch. f. Elektrotechn. und Electrochemie, i. 1894, p. 354) also publishes studies on the electrolytic formation of hypochlorites and chlorates. He points out that, according to the equations for forming those salts, equal molecules of caustic alkali and chlorine act upon each other, and that consequently it must be best to work without a diaphragm. His experiments were indeed made without one. He laid special stress on the analyses of the *gases*, comparing the mixture of hydrogen and oxygen, generated in a voltameter placed in the circuit, with the gases formed in the decomposing-cell itself, which ought to consist only of hydrogen, but which contain also a little chlorine (escaping at the beginning of the process) and oxygen (formed by secondary electrolysis of hypochlorite or chlorate). Suppose we have obtained in the voltameter 60 c. c. gas, which must be 40 c. c. H + 20 c. c. O. If we obtain at the same time in the decomposing cell 32 c. c. gas, containing 30 c. c. H, 1.6 c. c. O, and 0.4 c. c. Cl, we may conclude as follows:—From 30 H we must deduct that which corresponds to O and Cl, as not being available, which leaves  $30 - (3.2 + 0.4) = 26.4$  c. c. This indicates the actual efficiency of the current  $= \frac{26.4}{40} = 66.0$  per cent. The hydrogen deficit  $40 - 30 = 10$  indicates the hydrogen consumed by the undesirable reduction of hypochlorite, or a loss of  $\frac{10}{40} = 25$  per cent. of the current. The remaining 9 per cent. loss is caused by  $\frac{8.2}{40} = 8$  per cent. decomposition of water and  $\frac{0.4}{40} = 1$  per cent. of a mixture of Cl and H (detonating gas).

Oettel's experiments were at first made at the ordinary temperature with a 20-per-cent. solution of KCl, in order to produce essentially *hypochlorite*, with current-densities varying from 146 to 1460 amps. per square metre both at the cathode and the anode. The losses by reduction were very considerable, so that the current efficiency sometimes fell to 17 per cent.; especially injurious is a low current-density at the cathode. The best results were obtained with *high* current-densities (1460 amps. at both electrodes), viz., on the average 55 per cent., but tending towards a permanent maintenance of 30 per cent. current efficiency.

Chlorate was always formed together with the hypochlorite. The greatest attainable concentration was 12·7 grams available (bleaching) chlorine per litre; when this limit has been reached, a further supply of current causes the formation of chlorate.

The chlorate itself is hardly at all decomposed by the current, not even at 75°, as it is altogether very stable in an alkaline solution. The considerable losses in the shape of free oxygen are almost exclusively caused by the decomposition of hypochlorite, which, as shown by experiments, is only very imperfectly converted into chlorate when boiled by itself for a long time (comp. p. 516). In order to bring about this conversion free chlorine must act upon the hypochlorite, free hypochlorous acid being formed as an intermediate product. (Oettel here gives exactly the same explanation of the formation of chlorate as is found in the first edition of this book, vol. iii. p. 304, and repeated above, p. 513.) Hence the process must be explained as follows:—During the electrolysis at first KOH and Cl are formed, which unite to form KClO. The movement of the liquid carries this also to the cathode, where much of it is reduced to KCl. The remainder accumulates up to a percentage of at most 17 grams KOCl (=13 grams available chlorine) per litre. Upon this hypochlorite the chlorine formed at the anode acts and forms chlorate, the chlorine being always regenerated. Hence the following conditions ought to be fulfilled:—

1. Keeping the hypochlorite away from the cathode, to avoid reduction.
2. Avoiding the supply of fresh KOH to the anode before the hypochlorite has been transformed into chlorate.

Both conditions are attained in Gall and Montlaur's process, the former by employing a diaphragm; but in his laboratory experiments Oettel attained a yield of 82½ per cent. even without a diaphragm. He is uncertain as to whether it will ever be possible to attain such a yield with the old method, where chlorine acts upon milk of lime. The only possible anode is platinum, carbon is quickly destroyed, and produces a colouring-matter obstinately clinging to the potassium chlorate.

Further investigations by Oettel (*ibidem*, p. 474) showed that in electrolyzing strongly alkaline solutions a direct formation of chlorate takes place, without the intermediary formation of hypochlorite, which means an almost complete avoidance of the injurious reducing action of the current. This action was connected with an

active decomposition of water, and hence with evolution of oxygen. It seems to be most favourable if 30 per cent. of the current is spent on the decomposition of water and 70 per cent. on the formation of chlorate. Raising the percentage of alkali to 4 per cent. KOH causes the reduction of chlorate to be diminished to only 0.5 per cent.; in the final liquor there is only 5 bleaching chlorine to 95 chlorate-chlorine. Raising the temperature acts in a similar way as increasing the alkali, but in this case the decomposition of water increases, and hence the total current efficiency decreases.

The current-density at the cathode must be very great, as a low density favours the reducing action of the current. At the anode a diminution of the current-density produced an increased decomposition of water. There is an intimate connection among the three factors: alkalinity, temperature, and current-density; if two of these are fixed, it is possible by suitably choosing the third to attain always about the same favourable conditions for forming chlorate. If, for instance, we have to work in the cold and with high current-density, we must make the liquor strongly alkaline; if, on the other hand, a hot and weakly alkaline liquor has to be employed, the current-density at the anodes must be made less, and so forth. It is always best to cause a *direct* formation of chlorate by the addition of alkali. Since the electrical reduction losses are caused almost entirely by the hypochlorite, and the formation of the latter is very slight in an alkaline solution, it is possible to *dispense with the employment of a diaphragm*. It is certainly necessary to employ platinum anodes, and therefore the current-density at the anodes must be chosen as high as possible. Assuming the voltage in the bath = 3.3, and the current efficiency = 52 per cent., we arrive per hour, with an I.H.P. of 736 amps., at a production of 88.14 grams  $\text{KClO}_3$ , *i. e.*, 1 kilogram  $\text{KClO}_3$  requires work equal to  $11\frac{1}{3}$  effective horse-power hours.

The formation of *sodium chlorate* takes place similarly to that of the potassium salt; but the presence of NaOH promotes the formation of chlorate even more than the equivalent of KOH. On the other hand, the decomposition of water is increased, as the sodium chlorite does not precipitate, and by its accumulation participates in an ever increasing proportion in the conduction of the current. It is quite different in the case of *calcium chlorate*, where current efficiencies up to 87 per cent. can be attained.

The Elektrizitäts-Aktiengesellschaft vormals Schuckert (Germ.

pat. No. 83536) state that several drawbacks are avoided and the yield of chlorate is considerably increased by preventing the presence of caustic alkali at the anode, and producing the necessary alkalinity by the presence of carbonates. A solution of potassium chloride, saturated at the ordinary temperature, to which 2 or 3 per cent. of potassium bicarbonate are added, is electrolyzed in earthenware or iron vessels, with platinum or carbon electrodes (the carbon is not acted upon by the alkaline carbonate), carbon dioxide being passed in from time to time. The temperature should range between  $40^{\circ}$  and  $100^{\circ}$  C.; the current-density between 500 and 1000 ampères per superficial metre. The production of chlorate is greatest at first and gradually diminishes; hence the process is interrupted after some time, and the solution is drawn off and cooled down; most of the potassium chlorate crystallizes out, and the mother liquor is re-introduced into the process. In the case of sodium chlorate the liquor is boiled down; the NaCl which separates is fished out during the evaporation, and is employed for preparing a fresh solution for electrolysis. On cooling the mother liquor,  $\text{NaClO}_3$  is obtained by crystallization.

The manufacture of chlorate of potash by electrolysis on a very large scale is an accomplished fact. As mentioned, p. 720, the French Company, working the Gall and Montlaur patents, has carried on that manufacture for several years past at Vallorbes, with 3000 H.P., and a still larger plant is in course of erection in Savoy. The Mansbo Chemical Works in the province of Dalarne, in Sweden, have erected a plant for chlorate of potash by means of a waterfall furnishing 4000 H.P., of which at present 8 turbines at 220 H.P. are utilized, coupled directly with the dynamos. The dynamos work regularly with 115 volts and 1200 amps.

Other plants are said to be working or in course of erection in various places, but nothing certain can be reported thereon.

## CHAPTER XXX.

## SPECIAL FORMS OF ELECTRODES AND DIAPHRAGMS.

In the preceding chapters we have already met with numerous special forms of electrodes and diaphragms, which in many cases are the essential point of the apparatus in question. In referring to this, we shall in the present chapter mention a number of proposals made for preparing suitable electrodes or diaphragms, without having regard or being restricted to any special apparatus.

## ELECTRODES.

Usually it is the *anodes* which cause difficulties, as the chlorine is given off in contact with them, which causes such great strain upon them, that most materials are from the outset excluded. The generally used material is some kind of *carbon*, the denser the better, both for conductivity and for resistance to chlorine. The most usual material is "retort-carbon" from gas-works, but some artificially prepared carbons are also very good.

Worse even than the effect of chlorine upon carbon anodes is that of the *oxygen* given off by secondary reactions, or otherwise present. Sometimes the amount of carbon dioxide formed in this manner is so large that the chlorine has to be purified from it before it can be employed for the manufacture of bleaching-powder, *e. g.* by means of lime, which is thus converted into weak bleach.

Fitzgerald and Falconer (Engl. pat. 1246, 1890) describe under the name of "lithanode" a kind of electrode which is to replace platinum or carbon, and is neither acted upon by chlorine nor crumbles during use. These anodes consist of lead peroxide, and are especially intended for use in decomposing calcium or magnesium chloride. Patent No. 9799, 1892 (p. 683), refers to this.

Henneton's anode (Germ. pat. 68318) consists of a frame made of well-conducting material, insulated towards the bath, by which the current is conducted; in this frame wires of well-conducting,



refractory material are fixed, which serve for forming the surface of the anode. The frame is covered with gutta-percha, glass, &c.

Richardson (Engl. pat. 19953, 1892) prepares retort-carbon for anodes in the following manner:—Pieces of approximately equal size are selected, and if necessary are roughly dressed by means of a hammer. They are then notched or drilled to receive a metallic joint, produced by casting lead into the place of junction, which by its contraction on cooling produces an intimate contact of the metal with the carbon. The patent gives several drawings of such contacts.

Liveing (Engl. pat. 3743 & 3744, 1893) ignites the retort-carbon in a current of chlorine, so as to remove any hydrocarbons. In order to prepare anodes, he places pieces of retort-carbon on a sieve or grid made of a non-conducting material, such as slate; the anode chamber is closed at the top, and carbon rods pass in stuffing-boxes down to the layer of carbon lying on the grid. Since these rods wear out at the ends, they are pressed downwards in their stuffing-boxes by means of springs or weights.

Castner (Engl. pat. 19809, 1893) heats retort-carbon by the electric current, surrounding it with ground charcoal, or otherwise protecting it from being burned. A current of 350 to 500 amps. raises a carbon rod an inch square to a dazzling white heat in a few minutes. The retort-carbon during this process yields a little combustible gas, loses from 3 to 7 per cent. weight, increases its bulk a little, and gains in electric conductivity.

Gerard and Street (Germ. pat. 78926) propose making carbon electrodes more refractory in a similar way, by heating them in the electric arc, in order to convert them superficially into graphite.

*Carbon anodes with a liquid metallic core* are described by F. M. Lyte (Engl. pat. 7594, 1893). The carbon is tubular, closed at the bottom, and contains a core of lead, tin, or other metals or alloys, fusing at the same or a lower temperature than the metallic salt to be reduced, but not so low that any metal could be volatilized. In electrolyzing lead chloride, *e. g.*, lead is the proper metal. Into this fused core dips a rod of metal fusing only at a higher temperature (copper or iron), which fits loosely in the upper opening of the carbon, so that during the heating no pressure upon the lead is caused by the expansion of the metal; on this rod is the joint for the electric conductor (comp. p. 706).

*Ferrosilicium* had been previously proposed by Uelsmann for

cathodes in Bunsen batteries, where they have to resist nitric acid. Höpfner patented this material for anodes in lieu of carbon or platinum (Engl. pat. 9079, 1891). They are to be prepared by casting or cutting, or by electrolytic deposition on carbon, iron, &c. This is further developed in the German patent No. 77881. A siliceous melt is to be exposed to the electric current at a temperature near that of fusing cast-iron, a carbon rod serving as anode and an iron rod as cathode. The latter is then covered with a siliceous coating, which conducts the current very well and serves as an acid-proof anode.

*Phosphide of chromium*, pure or mixed with carbon, is proposed by Parker and Robinson for anodes (Engl. pat. 6007, 1892).

Oxidizing cathodes, made of *copper oxide*, are employed by Richardson and Holland (Engl. pat. 2296, 1890; 19704, 1891; comp. p. 661) and by Gibbs and Franchot (No. 4869, 1893; comp. p. 721).

Electrodes of special shapes occur, among others, in the previously-mentioned apparatus of Greenwood (p. 658), Rieckmann (p. 664), Craney (p. 666), Roubertie (p. 667), Faure (p. 668), Union Chemical Company (p. 669), Hargreaves and Bird (p. 669), Drake (p. 671), Kellner (pp. 683, 693, & 714), Parker (p. 683), Hermite (p. 687), Atkins and Applegarth (p. 689), Andreoli (p. 716), Spilker (p. 722), Vautin (pp. 698 & 702), Knöfler and Gebauer (p. 716), Gall and Montlaur (p. 720), Hulin (pp. 699 & 704).

#### DIAPHRAGMS.

*Asbestos* diaphragms are prepared by Roberts and McGraw (Engl. pat. 20111, 1890) as follows:—Asbestos cardboard is placed on both sides of an asbestos tissue, and the whole is covered with canvas, exposed for 24 hours to the action of hydrochloric acid of spec. grav. 1.09, squeezed out in the acid and rolled, thoroughly washed with water and flattened.

Waite (No. 2586, 1893) dissolves glue or isinglass in the smallest possible quantity of water, adds potassium bichromate 15 to 20 per cent. of the weight of the glue, stirs asbestos among the mass, and moulds the whole into sheets. Exactly the same thing is patented by Rieckmann (Germ. pat. 71378), who points out that bichromate-glue by itself is not sufficiently tough, and that it cannot be mixed with animal or vegetable fibre, which would be

soon destroyed; asbestos, however, is durable. The fixation of the bichromate-glue may be effected by exposure to light or by a bath of sodium thiosulphate.

Andreoli (No. 12662, 1893) describes diaphragms of asbestos, kieselguhr, or porous porcelain, tightly placed between iron or carbon cathodes, with carbon anodes. In order to protect the junctions from corrosion, the carbon is put in a hole of the cover with litharge cement; after making the metallic joint it is wrapped round with string and coated with paraffin.

Hargreaves and Bird (No. 18039, 1892) deposit a paste of asbestos, vegetable fibres, &c. on the inside of a vessel made of wire gauze or perforated metal, and produce on the top of this a second layer of a stone-like substance, as Portland cement or clay and silicate of soda. The metal of the vessel forms the cathode, and that portion of the diaphragm which directly touches it is made specially porous in order to promote the liberation of hydrogen.

According to No. 5198, 1893, they deposit on the wire gauze first a mixture of lime and asbestos, dry the whole, and dip into solution of silicate of soda, which produces an insoluble silicate, firmly adhering to the wire gauze. In No. 14131, 1893, they substitute sodium phosphate for the silicate, and describe some other modifications of the treatment.

Fig. 224.

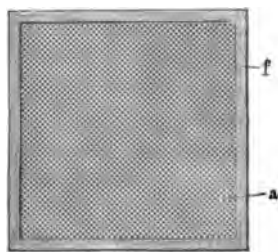


Fig. 225.



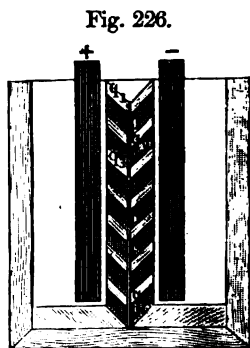
Wiernik (Zsch. f. angew. Ch. 1894, p. 298) employs asbestos tissue, of which two or more layers are put together; according to circumstances he places between these tissues thin layers of porous substances offering little resistance, such as asbestos fibre, kieselguhr, or china-clay, which are made to adhere by pressure

or otherwise. Fig. 224 shows such a diaphragm from the top, fig. 225 in section. It consists of three asbestos tissues, *a*, *b*, *c*, between which thin layers of asbestos fibres are placed at *d* and *e*. *f* is a bordering of tissue, &c., running round the edges of the diaphragm. These diaphragms are very thin and porous, and therefore conduct the electric current very well, but they are perfectly tight to liquids and gases and extremely durable; they are also sufficiently stiff and firm to be employed in practicable sizes without the assistance of insulating supports.

Waite (Engl. pat. 13756, 1894) protects asbestos diaphragms, resting on a wire-gauze cathode, by a layer of sand against leakage of hydrogen into the anode chambers, also against the corroding action of chlorine.

Riquelle (Germ. pat. 76704) makes porous cells by dipping pure asbestos tissue into boiling water, then coating them all over with a paste of china-clay, passing them between rollers, cutting them into pieces, pressing these into the shape of seamless hollow vessels, and finally burning in stoves like porcelain.

The Farbwerkevormals Meister, Lucius, and Brüning (Germ. pat. 73688) provide osmotic asbestos diaphragms on one or both sides with strips  $q, q_1, q_2, \dots q_n$  (fig. 226), resembling Venetian blinds, consisting of dense non-osmotic material. These strips run upwards in a sloping direction, so that the lowest point of any one strip is no higher than the highest point of the strip next below. This protects the osmotic plate against the gaseous products of decomposition, the gas-bubbles being forced upwards by the impermeable Venetian blinds; therefore a thin diaphragm, with small electrical resistance, admits of a sufficient separation of the products of decomposition.



Very similar to this is the plan of J. C. Richardson (Engl. pat. 12857, 1893).

Kiliani, Rathenau, Suter, and the Elektrochemische Works, Berlin (Engl. pat. 15276, 1894), construct acid- and alkali-proof diaphragms from permeable membranes, like parchment-paper, glass-wool, asbestos, cardboard, &c., held in frames between rows of parallel rods of acid-proof material, such as glass, porcelain, &c.

The rods are fixed in furrows or grooves of the square, circular, or oval frames. The membranes are tightly stretched round these frames, and are held fast by outer frames of the same material, by means of india-rubber rings or by coiling wire round them.

Rieckmann (Germ. pat. 80504) makes very durable diaphragms by covering the cathode with a thin asbestos cloth or cardboard, on which is placed an earthenware frame filled with fine sand, salt, or the like. This material penetrates into the asbestos, fills up the interstices, and forces it against the cathode, so that no gas can get in between and no displacement can take place. This prevents the entrance of hydrogen into the anode space and the formation of explosive mixtures of Cl and H.

Rieckmann (Germ. pat. 63116) also makes diaphragms from albumen, by pouring a solution of blood-albumen in two parts of water of 30° C. on to an oiled glass plate. This is covered with another similar plate, and the albumen is coagulated by dry steam in a stove, after which the plates are taken away. Stronger diaphragms are obtained by impregnating paper with the solution of albumen and coagulating this.

Höpfner (Germ. pat. 65656) makes diaphragms by coating felt, paper, leather, &c. with collodion and washing with water, whereby they are rendered porous.

Caldwell (Engl. pat. 21631) employs as diaphragms crystals of the salt to be electrolyzed, built up in a vertical mass between horizontal strips of glass, porcelain, &c. like Venetian blinds.

Breuer (Engl. pat. 19775, 1892) replaces the quickly worn-out earthenware diaphragms with others made of indestructible, porous *cement*. He gives several prescriptions for this:—(1) Sifted pieces of pumice or coke, 4 to 8 millimetres thick, are carefully mixed with their own weight of natural or artificial Portland cement, made with water into a thick paste and moulded; on setting, they are at once ready for use. The above-named size of the pumice or coke is suitable for diaphragms 10 to 15 millim. thick; for other thicknesses it must be varied. (2) 35 litres of ground rock-salt (or other soluble salt) are mixed with 65 litres of cement, made into a thick paste and lixiviated after setting. (3) 50 litres cement are mixed with 36 litres of a solution of 250 grams rock-salt in 1 litre water and 14 litres hydrochloric acid; otherwise the process is similar to No. 2. The rock-salt may be replaced by other

salts, the hydrochloric acid by other acids. (4) 100 litres cement are intimately mixed with 2 kilog. cut-up cow's hair or woollen yarn, made with water into a paste and moulded. Such diaphragms after moulding possess such porosity that they do not oppose any great resistance to the electric current; during use the hair or wool is gradually dissolved in the liquid, and the plates are rendered still more porous.

Carmichael (Germ. pat. appl. C. 5055, 1894) prepares porous cement diaphragms by impregnating a tissue (in the case of substances yielding chlorine an asbestos tissue) with Portland cement, moulding into plates, cylinders, &c., and drying. It is also possible to make a paste of the cement and the fibre and to mould this at will.

The Anciennes salines domaniales de l'Est (Germ. pat. 82352) employ diaphragms made of blocks of *limestone*, or made by moulding wet limestone powder and burnt magnesia into blocks by means of pressure. Such diaphragms in the electrolysis of alkaline chlorides offer very little electrical resistance, and are not at all acted upon by the products of electrolysis, so that they last practically for ever.

Parker (Engl. pat. 6605, 1893) makes very durable diaphragms from fluor-spar or cryolite, which are converted into a woolly material similar to slag-wool, and are then wrought into the form of tissues or employed in other ways for covering perforated vessels.

Bamberg (Engl. pat. 20413, 1891) avoids all porous diaphragms by employing a solid partition between the two chambers, with connecting pipes, the upper end of which is below the level of the liquid, while the lower end extends into the next chamber, so that no gases can pass through.

Häussermann (Zsch. f. angew. Ch. 1893, p. 393) draws attention, for use as diaphragms, to the very porous porcelain mass, absolutely resisting all chemicals, manufactured by Pukall at the Berlin Royal Porcelain Works (as described in Ber. d. deutsch. chem. Ges. 1893, p. 1159). Later on (Zsch. f. angew. Ch. 1894, p. 4) he published some experiments thereon. The Pukall cells are not visibly affected by digesting with 15 per cent. caustic-soda solution during four days at 90°; only very slight traces of alumina and silica are dissolved. Experiments with electrolyzing solutions of NaCl showed that the resistance of these cells diminished with

the rise of the temperature; especially when employing retort-carbon instead of artificial "electrical carbon," they yield much better results than ordinary earthenware cells.

Kellner (Engl. pat. 7801, 1894) proposes making diaphragms for electrolyzing solutions of NaCl of *soap*, which almost completely prevents the diffusion of caustic soda into the anode cell, as soap is insoluble both in solution of common salt and in caustic-soda solution. The soap is simply cast into plates of the desired size or else on to a substratum of glass-wool, or a soap plate is placed between two plates of asbestos cardboard or tissue.

Bein (Engl. pat. No. 21838, 1894) uses the intermediate layer of liquid formed during the electrolysis to keep separate the products of decomposition at the anode and cathode. This separating layer is rendered visible by suitable means, and when on the point of disappearing an impervious partition is introduced or the products of decomposition are drawn off.

The following patents, among those mentioned previously, contain the description of special kinds of diaphragms:—Greenwood (p. 658), Cutten (p. 661), Le Sueur (p. 662), Kellner (pp. 666 and 693), Roberts (p. 671), Hempel (p. 675), Marx (p. 678), Chemische Fabriken Leopoldshall (p. 682), Höpfner (p. 709), Hurter (p. 723).

## STATISTICS.

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FIRST of all we quote some statistics, in addition to those given in Vol. I., as to the consumption of *Brimstone* and *Pyrites*, and some other data referring to the manufacture of Sulphuric Acid, partly from Rothwell's 'Mineral Industry' for 1893, partly from Dammer's 'Handbuch der chemischen Technologie,' vol. i. (1895). So far as the statements contained in the last-named work are based on 'Commercial Reports' and on 'Estimations,' they must be used with great caution. Thus, *e. g.*, it is said that no pyrites whatever was consumed in Norway, whereas there is a sulphuric-acid works at Stavanger, burning pyrites, which I myself visited in 1890 and which is still in operation. The same holds good of Spain and Portugal, where there are well-known pyrites-consuming acid-works.

### BRIMSTONE.

Statistics up to 1888 are given in Vol. I. p. 17.

Production (in metrical tons).

	1889.	1890.	1891.	1892.	1893.
Sicily alone.....	327,672	328,024	347,568		
All Italy .....	371,494	369,239	395,528	418,535	417,671
Other Countries.....	50,326	61,488	61,605	56,638	
Total .....	421,820	430,727	457,133	475,173	



This does not comprise the sulphur recovered from Leblanc waste.

Of the above, 50,537 tons were refined in Italy alone in 1890, at 16 works.

The prices of Sicilian brimstone were, per ton :—

Year.	Lire.	Year.	Lire.
1860.....	120	1885.....	83
1865.....	123	1890.....	77
1870.....	121	1891.....	113
1875.....	142	1892.....	95
1880.....	100	1893.....	72

Exportation from Sicily to	1890.	1891.	1892.	1893.	1894.
	Tons.	Tons.	Tons.	Tons.	Tons.
France.....	73,596	58,262	77,424	91,722	51,648
Great Britain .....	28,701	26,682	24,739	25,286	20,108
Germany.....	15,611	12,067	18,668	17,531	14,912
Austria .....	16,594	15,491	13,499	13,807	10,427
Russia .....	14,388	12,753	11,186	19,174	16,308
United States and Canada .....	111,198	101,579	89,558	89,044	95,956
Other Countries.....	68,620	42,543	58,008	54,303	44,777
Total .....	328,708	269,377	291,082	310,867	254,136

The influence of the Chance-Claus process is very clear in the decline of the figures for Great Britain, which in 1883 imported 41,788 tons of brimstone from Sicily. In 1893 the importation was 25,757 tons, in 1894 23,396 tons.

Japan produced, in 1891, 44,505 tons of brimstone, 21,923 tons of which were refined. The exportation was :—

In 1890, 20,724, of which 17,807 went to the United States.			
„ 1891, 21,108,	„	19,068	„
„ 1892, 14,589,	„	11,446	„

The remainder went to China; Australia in 1894 took 2500 tons sulphur from Japan. The mines hitherto opened in the latter country seem to be nearly exhausted.

The production of brimstone in the United States was :—

In 1892.....	1,656 tons.
„ 1893.....	1,219 „
„ 1894.....	441 „

The same country imported brimstone (long tons) :—

Year.	Crude.	Flowers.	Refined.
1890.....	131,096	12	103
1891.....	116,971	206	10
1892.....	100,938	158	26
1893.....	107,601	241	41
1894.....	124,467	165	41

PYRITES (comp. Vol. I. pp. 32 *et seq.*, 884, 885).

*Great Britain and Ireland* (English tons) :—

Year.	Production.	Importation.	Consumption.
1890.....	16,018	656,891	672,909
1891.....	15,463	616,227	631,690
1892.....	14,000	604,411	618,411
1893.....	15,837	612,818	628,655
1894.....	15,523	616,050	631,573

The number of sulphuric-acid works in Great Britain and Ireland was :—in 1892, 226; in 1893, 219; in 1894, 212.

*France* (metrical tons) :—

Year.	Production.	Importation.	Exportation.	Consumption.
1890.....	229,661	39,553	15,908	253,306
1891.....	246,827	45,457	12,120	280,164
1892.....	230,480	47,502	22,455	255,527

*Germany* (metrical tons) :—

Year.	Production.	Importation.	Exportation.	Consumption.
1890.....	122,372	209,477	8,276	323,573
1891.....	128,248	238,644	9,393	357,539
1892.....	113,461	218,272	9,951	321,782
1893.....	121,334	274,766	15,889	380,211

*Production and Consumption of Pyrites in all Countries  
in 1890 (metrical tons) :—*

	Production.	Consumption.
Germany .....	122,372	323,573
Austria-Hungary.....	111,381	69,814
Belgium .....	5,051	28,831
Holland .....	0	8,820
France.....	229,661	253,306
Great Britain .....	16,018	672,909 †
Italy.....	14,755	14,755
Norway .....	56,000	? ‡
Sweden.....	1,135	2,135
Portugal .....	73,230	? ‡
Spain *.....	885,635	? ‡
Russia .....	16,000	18,200
Switzerland .....	158	3,658
United States .....	113,652	228,652
Canada.....	44,671	20,000
Other Countries .....	?	45,066
	<u>1,689,719</u>	<u>1,689,719</u>

**ZINC-BLENDE** (comp. Vol. I. p. 68).

The following are analyses of blende consumed at Rhenish acid works (by Minor) :—

Sulphur .....	30·24	27·94	22·11	21·05
Zinc as ZnS .....	27·73	27·17	34·46	31·16
„ in other forms.	5·03	4·75	5·83	6·65
Iron .....	15·98	13·12	2·06	2·33
Gangue (by diff.) ...	21·02	27·02	35·54	38·18

The average sulphur contained in the blende worked in Germany is 26 per cent. S.

\* To this should be added 1,271,000 tons roasted at the mines, the gases escaping into the air.

† Comp. the remark p. 738, concerning the statements taken from Dammer.

‡ In 1894 the amount of pyrites cinders treated in Great Britain for copper was 309,268 tons, the yield being 14,013 tons of copper, 1,790 ounces of gold, and 311,413 ounces of silver.

The production of blende in Prussia was :—

In 1890.....	362,464 tons.
„ 1891.....	378,082 „
„ 1892.....	407,987 „

In 1894, 160,000 tons blende were worked in Prussia for sulphuric acid.

#### PRODUCTION OF SULPHURIC ACID.

Jurisch (Dammer, vol. i. p. 206) calculated the production of Sulphuric Acid in the *German Empire*, expressed in tons of real  $H_2SO_4$ , as follows :—

Year.	From Pyrites.	From mixed Ores.	From Blende.	From Brimstone.	Total.
1890.....	391,211	34,120	58,820	7,810	491,961
1891.....	435,950	33,000	60,000	7,500	536,450
1892... ..	394,400	33,000	62,000	7,000	496,400

(In 1893 the total production was 506,624 tons.)

The same author calculates the total production of the world in 1890, based partly on somewhat doubtful assumptions (apparently rather too high) :—

In Europe.....	2,152,000 tons real $H_2SO_4$ .
„ America .....	665,000 „ „
	<hr/> 2,817,000

*The Consumption of Sulphur in the United States* from all sources in 1893 is stated in Rothwell's 'Min. Ind.' 1894, p. 547 (in English tons) :—

	Cont. real Sulphur.
107,661 tons brimstone imported .....	105,508
1,200 „ „ mined in the country. ....	1,176
221,000 „ pyrites imported .....	106,080
95,000 „ „ mined in the country ...	42,750
Total.....	<hr/> 255,514

(This does not mention zinc-blende, which, as I have myself noticed, is employed in large quantities for the production of sulphuric acid in the United States.)

Compare also later on the statistics given in connexion with soda.

In *Italy* (Candiani, Chem. Ind. 1895, p. 153) there were in 1895 24 sulphuric-acid works, with a total chamber-space of about 4 million cubic feet, half of which produced acid only for their own consumption (for superphosphate). All of them worked with pyrites, some of which is imported from Spain.

#### STATISTICS OF THE SODA INDUSTRY.

The statistical data, given in the first edition of this book, Vol. III. pp. 67 to 75, will not be repeated here, although these older figures are not at all devoid of interest; we shall here confine ourselves chiefly to more recent statistics.

#### *Great Britain and Ireland.*

The quantities of salt employed in the Leblanc and ammonia soda processes during the years from 1862 to 1892 have already been quoted (Vol. II. p. 16). We here give the figures for 1893 and 1894:—

	1893.	1894.
Used for saltcake and in the Leblanc process.....	467,562	434,298
Used in the ammonia-soda process..	349,609	361,603
Total.....	817,171	795,901

Showing, again, a decline since 1890, when the consumption of salt was at the maximum of 855,029 tons. The consumption of salt for ammonia soda is still on the increase, but that consumed in the Leblanc process is smaller than in any year since 1874.

There were 71 alkali-works in Great Britain in 1894.

The production of *soda* in different forms and that of *bleaching-powder* (comprising its equivalent of *chlorate of potash*) are taken from the data collected by the British Alkali Makers' Association. Unfortunately these are not accessible since 1887, even by special inquiries. The soda-ash is all reduced to 48° (= 82 p. c.  $\text{Na}_2\text{CO}_3$ ),

the caustic to 60° (=102·6 p. c. Na<sub>2</sub>CO<sub>3</sub>). The figures indicate tons.

Year.	Leblanc Soda-ash, 48°.	Ammonia Soda-ash, 48°.	Soda Crystals, 21°.	Caustic Soda, 60°.	Bicar- bonate, 38°.	Bleaching- Powder and Chlorate of Potaash.
1877.....	217,556	6,220	169,769	74,663	12,109	105,529
1878.....	196,876	11,116	170,872	84,642	11,756	105,044
1879.....	230,683	15,526	185,319	86,511	13,083	115,290
1880.....	266,093	18,800	192,926	106,384	13,539	131,606
1881.....	238,687	20,400	203,773	108,310	12,853	135,826
1882.....	233,213	39,000	180,846	116,864	14,115	135,170
1883.....	227,284	52,750	188,678	119,929	13,609	141,868
1884.....	204,072	61,480	182,567	141,639	14,576	128,651
1885.....	184,597	77,530	202,705	144,954	15,179	132,761
1886.....	165,782	85,000	182,379	153,884	15,083	163,234
1887.....	255,272		...	169,463	...	139,925
1890.....	.....	.....	...	...	...	153,000

*Exportation of Chemicals from Great Britain.*

*Alkali in all forms:—*

	1893. Tons.	1894. Tons.	1895. Tons.
Russia.....	15,265	9,929	9,737
Sweden and Norway ...	6,665	6,787	7,984
Germany .....	6,715	6,367	5,610
Holland .....	4,470	5,269	6,647
France .....	2,860	2,317	2,139
Spain .....	11,560	15,407	15,995
Italy .....	9,955	10,789	11,721
United States .....	173,325	166,834	176,248
Australia .....	7,085	11,532	9,958
British North America...	10,820	11,718	10,776
Other Countries .....	43,415	52,022	56,181
Total .....	291,635	298,971	312,996

*Bleaching-Powder :—*

	1893. Tons.	1894. Tons.	1895. Tons.
United States .....	39,330	39,327	44,537
Other Countries .....	27,055	25,216	26,188
Total.....	66,385	64,543	70,675

*Chlorate of Potash :—*

Japan alone took, in 1893, 1,504 tons from England, only 54 tons from Germany, and 17 tons elsewhere.

*Prices in England, per ton (Liverpool).*1. *Soda-ash (48°) :—*

	£	s.	d.	
1830.....	26	10	0	
1839-40 .....	15	0	0	
1878.....	5	10	0 to £6	0 0
1886.....	4	0	0	
1891.....	4	15	0	

2. *Soda Crystals :—*

£	s.	d.	£	s.	d.
1800.....	44	10	0	1860.....	6 15 0
1810.....	59	10	0	1868.....	4 2 6
1820.....	36	10	0	1878.....	3 12 6
1830.....	18	5	0	1886.....	2 15 0
1840.....	10	2	6	1889.....	2 2 6
1850.....	5	10	0		

3. *Bleaching-Powder :—*

£	s.	d.	£	s.	d.
1799.....	168	0	0	1868.....	10 12 0
1805.....	120	0	0	1878.....	5 0 0
1815.....	80	0	0	1886.....	5 17 6
1830.....	20	0	0	1891.....	6 10 0
1850.....	13	15	0		

*Germany.*

The extent of the German soda industry cannot be inferred from the official statistics of the production of salt, as these quote only the solid salt converted into saltcake and Leblanc soda, but not the very large quantities of brine directly entering into the ammonia-soda process, which are included in the British statistics.

The *total production* of soda in all forms is estimated in successive communications by Hasenclever as follows, reducing all the data to tons of 100 per cent. sodium carbonate (=58·5 per cent. real  $\text{Na}_2\text{O}$ ), which makes them appear much too small if compared with the British Alkali Makers' data (p. 744), where soda-ash is reduced to 48 per cent., crystals to 21 per cent., caustic to 60 per cent., and bicarbonate to 38 per cent.  $\text{Na}_2\text{O}$  :—

Year.	Leblanc Soda.	Ammonia Soda.	Total.
1877 .....	.....	.....	42,500
1883 .....	56,200	59,100	115,300
1890 .....	30,000	165,000	195,000
1894 .....	40,000	210,000	250,000

The steady rise of the soda industry in Germany is very clearly illustrated by the table on p. 747, expressed in metrical tons, compiled from the official statistics of exportation and importation, which have been rendered more simple by reducing all alkali products in the last column to 100 per cent. sodium carbonate. The table shows for every year the excess of importation over exportation, or *vice versa*. Taking only the grand totals, summarized in the last column, we find the maximum excess of importation over exportation, about 27,000 tons, in 1876 to 1878. In 1884 the scale inclines the other way, and has now arrived at about 40,000 tons excess of exportation over importation. But this difference, considerable as it is, does not by far represent the real development of the soda industry in Germany, since the internal consumption of alkali in that country has enormously increased during the period over which these data extend (comp. Hasenclever's estimates, *suprà*).



Year.	Soda-ash.		Caustic Soda.		Soda Crystals.		Bicarbonate.		Total reduced to 100 p. c. $\text{Na}_2\text{CO}_3$ .	
	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.
1872	7,513	...	1,331	...	10,977	...	238	...	12,241	...
1873	10,104	...	1,858	...	12,306	...	472	...	16,083	...
1874	15,413	...	3,751	...	11,040	...	404	...	22,638	...
1875	16,084	...	5,980	...	11,381	...	517	...	26,104	...
1876	14,212	...	7,831	...	13,253	...	503	...	27,500	...
1877	14,530	...	7,985	...	10,679	...	510	...	26,787	...
1878	14,111	...	9,275	...	9,219	...	452	...	27,474	...
1879	16,911	...	6,887	...	10,086	...	366	...	26,475	...
1880	6,061	...	9,373	...	10,053	...	263	...	20,512	...
1881	6,310	...	5,266	...	10,833	...	327	...	16,132	...
1882	5,368	...	6,134	...	7,332	...	297	...	15,251	...
1883	887	...	4,748	...	2,076	...	206	...	7,917	...
1884	...	7,318	1,973	...	2,037	...	250	...	...	3,305
1885	...	8,602	2,259	...	283	...	112	...	...	6,270
1886	...	9,150	676	...	...	1,759	120	...	...	10,304
1887	...	14,095	33	...	...	1,818	150	...	...	15,730
1888	...	16,186	103	...	...	1,959	231	...	...	17,925
1889	...	18,860	112	...	...	1,199	379	...	...	19,548
1890	...	26,083	...	...	...	1,735	163	...	...	28,465
1891	...	35,131	...	810	...	7,785	37	...	...	40,520
1892	...	34,431	...	2,763	...	3,545	45	...	...	41,470
1893	...	29,013	...	5,402	...	2,254	90	...	...	34,622
1894	...	32,805	...	4,532	...	1,346	...	...	...	40,089
	...	...	...	6,230	...	...	...	33	...	...

The corresponding figures for the excess of importation over exportation, or *vice versa*, into Germany for *bleaching-powder* are as follows (in metrical tons) :—

Year.	Import Excess.	Export Excess.	Year.	Import Excess.	Export Excess.
1882.....	5,440	...	1889.....	3,907	...
1883.....	4,456	...	1890.....	6,093	...
1884.....	5,441	...	1891.....	2,074	...
1885.....	5,747	...	1892.....	...	626
1886.....	5,330	...	1893.....	...	1,534
1887.....	2,975	...	1894.....	...	2,178
1888.....	4,512	...			

*France.*

The following quantities of salt have been used in the manufacture of saltcake and soda (metrical tons) :—

Year.	Saltcake and Leblanc Process.	Ammonia Process.	Total.
1878.....	117,015	32,891	149,906
1879.....	118,770	43,640	162,410
1880.....	125,317	47,952	173,269
1881.....	127,230	60,023	187,253
1882.....	123,911	72,174	196,085
1883.....	125,655	85,854	211,509
1884.....	125,695	97,491	223,186
1885.....	126,990	120,551	247,541
1886.....	120,001	141,181	261,182
1887.....	112,024	152,202	264,226
1888.....	107,020	155,902	262,922

Excess of importation over exportation, or *vice versa*, in France, in metrical tons :—

Year.	Soda-ash.		Caustic Soda.		Black-ash and Nat. Soda.		Soda Crystals.		Bicar-bonate.		Bleaching-Powder.	
	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.	Imp. Excess.	Exp. Excess.
1889 ...	...	4,819	3,286	...	...	1,435	...	26,865	100	...	...	...
1890 ...	...	2,759	1,705	...	...	170	...	29,190	337	...	...	...
1891 ...	...	1,119	...	237	...	2,595	...	25,343	539	...	...	4,453
1892 ...	...	1,859	...	268	...	1,072	...	26,400	549	...	...	8,227

In *Chlorates* there was no importation, the exportation was in tons :—

	1889.	1890.	1891.	1892.
Chlorate of potash.....	200	135	254	129
„ soda and baryta.	183	171	272	284

*United States of America.*

The following estimate for the fiscal year ending May 1, 1890, is given in the 'Oil, Paint, and Drug Reporter,' 1895, No. 6, p. 24 c, as to the total production in the United States :—

	lbs.	Metr. tons.
Soda-ash .....	98,801,200	38,204
„ crystals .....	144,641,705	58,290
Bicarbonate .....	60,678,750	24,453
Caustic Soda.....	33,002,720	13,299
Sulphuric Acid, 50° B...	1,009,683,407	406,901
„ „ 60° B....	20,379,908	8,213
„ „ 66° B....	354,533,657	142,863

(The figures for bicarbonate appear extremely high.)

Mr. R. P. Rothwell (private communication) estimates the total output of alkali, reckoned as 58 per cent. ash, in 1895=about 161,000 tons, and believes that in three years it will exceed 300,000 tons.

Rothwell's 'Mineral Industry,' iii. p. 98, gives the following figures for the imports of chemicals into the United States (in pounds):—

Year.	Soda-ash and Crystals.	Caustic Soda.	Bicarbonate.	Bleaching-Powder.
1890 .....	360,521,656	88,345,462	916,355	105,696,046
1891 .....	347,822,902	68,154,226	1,500,663	108,880,831
1892 .....	361,648,637	54,384,120	1,466,595	109,888,561
1893 .....	348,972,506	52,116,492	1,360,426	98,618,147
1894 .....	219,517,064	46,554,322	.....	96,256,251

Chlorate of potash : 1893 ..... 3,881,791 lbs.

„ „ 1894 ..... 4,599,969 „

In 1895 several lots of caustic soda were actually exported from America (by the Solvay Processes Co.) to England; but this was only in consequence of a temporary disarrangement of the trade, inasmuch as the United Alkali Co. was then selling caustic soda in England at from \$10 to \$14 a ton more than in New York.

### *Total Production of the World.*

#### *I. Soda of all kinds.*

Weldon (Journ. Soc. Chem. Ind. 1883, p. 2) estimated the production in 1882, calculated in tons of pure  $\text{Na}_2\text{CO}_3$ :—

	Leblanc Process.	Ammonia Process.	Total.
England .....	380,000	52,000	432,000
France.....	70,000	57,125	127,125
Germany.....	56,500	44,000	100,500
Austria .....	39,000	1,000	40,000
Belgium .....	.....	8,000	8,000
United States.....	.....	1,100	1,100
	545,500	163,225	708,725

Since then the state of affairs has very much changed, as is

apparent from the special statistics given above. In Great Britain the production has not greatly increased, in France it has decidedly done so; in Germany it has far more than doubled (p. 746); and the United States have only entered the field since that time (p. 749). The present production of the world must exceed the equivalent of a million tons of pure sodium carbonate.

## II. *Bleaching-Powder and Chlorates.*

Eschellmann (Chem. Ind. 1889, p. 2) estimates the production in 1888:—

### *Bleaching-Powder.*

	Tons.		Tons.
England .....	142,605 = Chlorine		49,912
Continent .....	40,000 = „		14,000
	<hr/>		<hr/>
	182,605		63,912

### *Chlorates.*

	Tons.		Tons.
England .....	6,000 = Chlorine		1,737
Continent .....	1,500 = „		435
	<hr/>		<hr/>
	7,500		2,172

### *Hydrochloric Acid (32° Tw.).*

	Tons.		Tons.
Germany .....	148,450 = Chlorine		49,000
			<hr/>
Total Chlorine.....			115,084

This amount of chlorine, contained in the final products, corresponds to 300,000 tons chlorine in the raw materials.

Kolb estimates the total production of bleaching-powder in Europe in 1892 = 220,000 tons.

## ADDENDA

TO VOLS. I., II., AND III. OF THE SECOND EDITION.

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VOL. I. p. 16. *Production of Sulphur in Sicily*.—According to Chem. Trade Journ. xiv. p. 320, the Gill kilns are rapidly gaining ground in replacing the calcareous methods, and they increase the output of sulphur by 50 per cent. These kilns consist of an oven, covered by a cupola, called a "cell;" inside there is a smaller cupola, within which a coke fire is burning. Each cell holds from 5 to 30 cubic metres of ore. There are generally six cells working in an angular battery. The gases generated in the first cell pass by lateral channels into the next; by the time the fusion is completed in the first cell, the contents of the second cell are already heated up to the igniting point by the gases, and so on. The gases heavily charged with sulphur are not lost as in the calcarone method; the yield is much larger, the time shorter (three or four days for each cell), and as the quantity of smoke is much less, the work can be continued almost all the year round without danger to the crops. In 1888 there were only 365 cells in 40 mines, in 1894 already 1821 cells in 225 mines, that is over two-thirds of the total.

A Report of the Italian Minister of Agriculture for the year 1894 (Chem. Ind. 1895, p. 182) describes the depressed state of the Sicilian sulphur industry.

VOL. I. p. 18. *Occurrence of Sulphur*.—According to Chem. Ind. 1892, p. 443, the layer of sulphur at Tschirkat in Daghestan is worked to the extent of 300,000 pud (at 40 lbs.) per annum; the selling price is 1·18 roubles per pud.

According to Chem. Zeitg. 1894, p. 2002, a large bed of brimstone has been found in Transcaspia, 60 versts from the port of

Usun-Ada on the Caspian Sea, only 2 versts from a railway-line. The bed is just below the level of the ground and is worked by open quarrying. The ore contains from 35 to 40 per cent. sulphur, and costs 20 to 25 copeks at Usun-Ada. If the results expected were realized, Russia would become entirely independent of Sicilian sulphur.

*Extraction of Sulphur in Russia.*—Chonski (Chem. Zeit. 1895, Repert. p. 411) reports on the production of sulphur, which has been tried in several places in Russia, but has been everywhere discontinued. He enumerates the drawbacks connected with the various methods for extracting sulphur from the raw ore. This paper should be consulted by those who consider any newly discovered vein of sulphur ore as being equal to ready money.

Vol. I. p. 21. *Extraction of Sulphur from spent Oxide of Gas-works.*—Broadberry (Gas World, 1895, xxiii. p. 643) extracts the sulphur from spent oxide of gas-works by means of benzol at a temperature of 70° or 80° C., employing a circulating-apparatus. 1 gallon of hot benzol yields on cooling 2·5 to 2·75 lbs. of solid sulphur, and retains 0·25 lb. in solution which is obtained in distillation. From an experiment with 20 lbs., he calculates a profit of £1 6s. 3d. per ton of spent oxide.

Vol. I. p. 21. *Sulphur from Pyrites.*—Buisine (Germ. pat. 73222) heats half-roasted pyrites with sulphuric acid, to recover sulphur, ferrous sulphate being obtained as by-product. According to pat. 79706, the pyrites is to be distilled in closed vessels at 700° C. and the residue treated as above with sulphuric acid. The residue, consisting of sulphur and ferrous and cupric sulphate, can be applied as it is to vines for certain diseases; or else it is extracted with water, the residue is worked for sulphur, and the solution, by treating it with metallic iron, yields metallic copper and ferrous sulphate.

Vol. I. p. 27. *Different behaviour of Pyrites and Marcasite.*—Detailed investigations on this point have been published by A. P. Brown (Chem. News, 1895, lxxi. p. 139 and following numbers).

Vol. I. p. 41. *Pyrites in Italy.*—Candiani (Chem. Ind. 1895, p. 153) gives a survey of the Italian occurrences. In Sicily excellent pyrites has been discovered. The whole of the 24 Italian sulphuric-acid works burn pyrites, partly imported from Spain, to the exclusion of brimstone.

Vol. I. p. 43. *Pyrites in Norway*.—The Vigsnaes mines are nearly exhausted; those still working are: Sulitjelma (by Bodoe); Bosmo (by Trondhjem); det Bergenske Grubeselskab, Stordoen by Lervik; Roraas Kobbervark (Trondhjem).

Vol. I. p. 47. *Analyses of American Pyrites* are given by K. F. Stahl (Zsch. f. angew. Chem. 1893, p. 54). No. 1 is from Tallapoosa Mine, Georgia, 1882; No. 2 from Rogers Mine, Paulding Co., Dallas, Ga.; No. 3 from Sulphur Mines Co. of Virginia, Louisa Co., 1884; No. 4, Peru Zinc Co., La Salle, Ill.; No. 5 from Dodgeville, Wis.; No. 6, from the same mine as No. 3, 1891; No. 7, Davis Sulphur Ore Co., Franklin Co., Mass., 1891.

	1.	2.	3.	4.	5.	6.	7.
Water .....	—	—	2.9	—	—	1.3	0.8
Sulphur.....	45.1	37.6	37.1	50.2	43.7	40.6	42.4
Iron .....	—	40.6	41.5	—	—	37.3	35.4
Copper .....	3.1	5.2	0.6	—	—	1.0	1.4
Zinc .....	3.0	4.5	0.8	—	—	1.9	5.5
Cadmium .....	0.1	0.01	?	—	—	?	?
Insoluble .....	2.9	9.5	14.7	—	1.4	10.5	5.1
Arsenic .....	?	?	0.02	—	—	trace	trace

Vol. I. p. 57. *Estimation of Sulphur in Pyrites*.—Gladding (Chem. News, 1895, lxx. p. 181) describes some alleged improvements in my method, which I have proved not to be such in Zsch. f. angew. Chem. 1895, p. 69, and in the Journ. Amer. Chem. Soc., March 1895.

Vol. I. p. 63. *Testing Pyrites cinders for Sulphur*.—In investigating Watson's method, I have found that it must be carried out with special precautions in order to yield accurate results. 3.200 grams of the finely ground sample are mixed with 2.000 grams sodium bicarbonate (of known alkalimetric titre), and heated in a nickel or iron crucible; a platinum crucible easily leads to over-heating. The heating is continued for 10 or 15 minutes with a very small flame, then another 15 minutes with a strong flame, but without fusing the mass. The crucible must be kept covered, and the mass must not be stirred; it should in the end be red-hot, and after cooling black and porous. It is boiled in a porcelain dish with water, adding the same volume of neutral solution of sodium chloride (without which addition some oxide of iron passes through the filter); the filtered solution is titrated with standard acid. The difference between the original



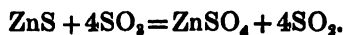
titre of the bicarbonate and that now found shows the sulphur, 1 c.cm. normal acid indicating 0·5 per cent. S. In the presence of a somewhat considerable quantity of zinc this method does not answer.

Vol. I. p. 67. *Acid smoke from chemical and other works.*—According to the 28th Alkali Report (for the year 1891), p. 19, the quantity of acid gas which escapes into the air at St. Helens, calculating the HCl as its equivalent of sulphur acids, is as follows:—

	Tons Sulphur per annum.	
From Copper and Lead smelting works.....	11,480	} 19,313
„ Glass-works.....	7,500	
„ Polishing-powder works.....	338	
„ Coal burnt (1½ per cent. of 1,040,000) ...	...	15,600
„ Chance-Claus process.....	...	620
„ Sulphuric-acid chambers .....	173	} 575
„ Alkali-works .....	402	
Total.....		36,108

This is the equivalent of 72,216 tons SO<sub>2</sub> or 110,586 H<sub>2</sub>SO<sub>4</sub>, of which the alkali-works contribute only 1½ per cent. Since all this is given off from an area of about 3 square miles, each square mile at St. Helens receives the equivalent of 12,036 tons sulphur, against 11 tons in summer or 44 tons in winter on a square mile in London.

Vol. I. p. 68. *Treatment of complex ores containing blende.*—Hart (Journ. Soc. Chem. Ind. 1895, p. 544) proposes treating such ores with sulphuric acid in a saltcake pot, and when the mass has become pasty transferring it to a blind roaster and finishing it there, all the gases going into vitriol chambers. The zinc remains behind as sulphate, which can be obtained by lixiviation and crystallization; or else it is mixed with poor zinc ore and roasted, in which case the oxygen of the sulphate combines with the sulphur of the blende. The reaction seems to be:



Vol. I. p. 70. *Spent oxide of gas-works.*—If this contains considerable quantities of cyanides, it may cause great trouble in the manufacture of sulphuric acid (31st Alkali Report, p. 89).

Vol. I. p. 73. *Utilization of Sulphuretted Hydrogen from sulphate-*

*of-ammonia works for the manufacture of Sulphuric Acid.*—This is no longer a rare exception, but is now practised in a good many English works, as shown in the 28th Alkali Report, p. 66. If the gas is properly introduced into the burner (comp. Vol. I. p. 277), the consumption of nitre is not excessive, and it is even possible to increase the heat by this means, if the spent oxides should not suffice for this purpose. The action of the large quantity of carbonic acid accompanying the  $H_2S$  in the case of sulphate-of-ammonium works would seem to consist only in requiring a certain amount of chamber-space, contrary to the opinion reported, Vol. I. p. 494.

Vol. I. p. 78. *Testing Nitrate of Soda.*—Gilbert (Zsch. f. angew. Chem. 1893, p. 495) points out that the Chilean nitre always contains, and always has contained, some potassium nitrate. Hence the warning recently raised against buying nitre by "refraction," which means paying partly for  $KNO_3$  instead of  $NaNO_3$ , and thus obtaining less nitrogen, is needless. The percentage of  $KNO_3$  rarely exceeds 5 per cent., and the deficiency of nitrogen caused thereby is more than compensated by the value of the potassium for agricultural purposes. The old method of testing for "refraction" is obstinately adhered to by the producers, and is practically very useful, even more so than the direct guarantee of 15.57 per cent. nitrogen demanded by the agricultural control-stations. Jones (*ead. loco*, p. 698) mentions that he had met with nitre containing much more potash; but this nitre, which is recovered from the bilge-water of the carrying vessels, occurs only quite exceptionally. [In these discussions the interests of agriculture are exclusively dealt with. Here the potash is certainly valuable as such, but the sulphuric acid or nitric acid manufacturer receives no benefit whatever from the potash, and for him the nitrogen estimation is exclusively important, as I have shown in Chem. Ind. 1883, p. 369; comp. Vol. I. p. 78. The recovery of nitre from the bilge-water of the ships conveying it, which had been carried on for a long time as a matter of course, forms the subject of a recent English patent!]

Vol. I. p. 78. A new bed of *nitrate of soda* has been found in Columbia (Journ. Soc. Chem. Ind. 1894, p. 1001). It is about 100 kilometres distant from San Juan de la Cienaga, and had been proved up to that time for a surface of 75 square kilometres. It has a thickness of from 30 centimetres to 3 metres, and averages 11 to 12 per cent.  $NaNO_3$ , together with calcium carbonate,

calcium sulphate, and silicates. The recoverable nitre is estimated to exceed 7 million tons.

Buchanan's description of the manufacture of nitrate of soda and iodine in Chili (Journ. Soc. Chem. Ind. 1893, p. 128) offers nothing of special novelty or interest for our purpose.

Vol. I. p. 84. *Influence of nitrogen tetroxide on the specific gravity of Nitric Acid.*—From a paper by Lunge and Marchlewski (Zsch. f. angew. Ch. 1892, p. 10) I give the following table, showing this influence in the case of nitric acid of spec. grav. 1.4960 (at  $\frac{15^{\circ}}{4^{\circ}}$ ).

$N_2O_4$ per cent.	Alteration of spec. grav. by $N_2O_4$ .	$N_2O_4$ per cent.	Alteration of spec. grav. by $N_2O_4$ .
0.25	0.00050	6.75	0.04475
0.50	0.00075	7.00	0.04650
0.75	0.00150	7.25	0.04720
1.00	0.00300	7.50	0.05000
1.25	0.00475	7.75	0.05165
1.50	0.00675	8.00	0.05325
1.75	0.00775	8.25	0.05500
2.00	0.01050	8.50	0.05660
2.25	0.01250	8.75	0.05825
2.50	0.01425	9.00	0.06000
2.75	0.01625	9.25	0.06160
3.00	0.01800	9.50	0.06325
3.25	0.01985	9.75	0.06500
3.50	0.02165	10.00	0.06600
3.75	0.02350	10.25	0.06815
4.00	0.02525	10.50	0.06975
4.25	0.02690	10.75	0.07135
4.50	0.02875	11.00	0.07300
4.75	0.03050	11.25	0.07450
5.00	0.03225	11.50	0.07600
5.25	0.03365	11.75	0.07750
5.50	0.03600	12.00	0.07850
5.75	0.03775	12.25	0.08050
6.00	0.03950	12.50	0.08200
6.25	0.04175	12.75	0.08350
6.50	0.04300		

Vol. I. p. 88. *Manufacture of Nitric Acid.*—Prentice (Engl. pat. 6960, 1893) carries on this process in a continuous manner. The nitre is mixed with sulphuric acid outside the retort, preferably in a kind of mortar-mill (according to patent No. 8902, 1893, a large excess of sulphuric acid should be employed and the residue subsequently used for the manufacture of superphosphate). The mud thus produced is conveyed into a heated chamber in

which the nitrate dissolves in the sulphuric acid, but no nitric acid is as yet split off [?]; here chlorine and nitrogen tetroxide are liberated and escape into a condensing-apparatus. Owing to this the nitric acid is later on free from volatile impurities [?]. The mixture is now charged into the retort, which has an oblong section and is divided into a number of separate chambers by partitions starting from the cover and not reaching entirely to the bottom. Above each chamber the cover is provided with a head and vapour-pipe. The retort is heated from below, and the fire-gas subsequently travels round the sides. The mixture coming from the heating-chamber enters the first chamber of the retort, where it begins to boil and gives off a large quantity of strong nitric acid mixed with a little nitrogen tetroxide. The mixture now, without ceasing to boil, flows on from chamber to chamber, giving off pure nitric acid, which gets weaker and weaker in the following chambers. In the last chamber, placed immediately above the fire, the temperature is highest; here the last nitric acid is driven off, together with much water and a little sulphuric acid, and the nitre-cake is drawn off, free from the nitrate. By this method  $\frac{3}{4}$  of fuel and  $\frac{2}{3}$  of condensing-plant [?] can be saved. A still producing 4 tons per week weighs less than two tons.—A communication by Prentice in the 'Journal of the Society of Chemical Industry,' 1894, p. 323, gives nothing new. In discussing it doubts were expressed as to whether that process is applicable at such works where the residue cannot be utilized for the manufacture of superphosphate.

Vol. I. p. 92. *Manufacture of Nitric Acid*.—The Griesheim Chemical Company (Germ. pat. 59099) place behind the retort a reflux cooler, consisting of a Rohrmann stoneware worm, contained in a water-tub kept at about 30° C. by the heat of the operation itself. The acid vapours ascending in this cooler are partially condensed here; in consequence of the high temperature the lower nitrogen oxides (together with the chlorine) escape in the state of vapour, and are condensed by air and water in a "Lunge tower" (plate-column) to weak nitric acid. The acid condensing in the worm flows into a receiver, kept at 80° C., and is therefore perfectly pure, no "bleaching" being required. Air is advantageously introduced here. [According to my own observations, this system works very well and on a very large scale.]

Vol. I. pp. 92 and 889. *Guttmann's apparatus for the condensation of Nitric Acid* are fully described in a communication

published in the Journ. Soc. Chem. Ind. 1893, p. 203. Further improvements are contained in a German patent by Guttman and Rohrmann, No. 73421. By means of an air-injector 94 per cent. of the theoretical quantity of nitric acid is recovered as 96 per cent. acid, and another 2 per cent. in the plate-column following the Guttman battery, as acid of 80° Tw., with only 1 per cent. as  $N_2O_4$ , and with consumption of 1 part of coal to  $3\frac{1}{2}$  parts of strong acid. The cooling-water in his "water-battery" amounts to 150 or 200 litres per double condenser, and the compressed air to about 2 cub. metres of 4 atmospheric tensions. The new battery costs only about half as much as the old (Zsch. f. angew. Chem. 1893, p. 39).

Oscar Guttman's work, 'The Manufacture of Explosives,' 1895, contains a very good account of the manufacture of nitric acid, with many illustrations.

Hart (Engl. pat. 17289, 1894) uses an apparatus similar in principle both to Guttman's and to the cooling-worms otherwise employed, consisting of a series of superposed glass tubes, slightly inclined to the horizontal, which starts from an upright stand-pipe and end in another upright pipe. The pipes are cooled by squirting water upon them or otherwise. The vapours pass simultaneously through all the inclined pipes. As the water squirted on to the glass tubes evaporates, its cooling-action is very strong. Hart asserts that by his method the distillation is effected in half the usual time, with very little fuel and slight formation of  $N_2O_4$ .

Valentiner (Engl. pat. 610, 1892) manufactures nitric acid in a *vacuum*. The retort in which the sodium nitrate is decomposed with sulphuric acid is connected with a cooling-worm, and this is connected with a receiver, from which, with the interposition of a Woulfe's bottle, the air is aspirated by an air-pump. In this way the most highly concentrated pure nitric acid can be obtained. [Perfectly pure nitric monohydrate, produced by this process, is now found in commerce. Before Valentiner (whose patent dates Sept. 8, 1891), I had shown that this can be done by distilling *in vacuo*, Zsch. f. angew. Ch. 1891, p. 167, published March 15, 1891.]

Hallwell (Chem. Zeit. 1895, p. 118) gives some details as to the practical application of the process. The cast-iron retort holds 16 cwt. of nitrate of soda and is nearly globular in form. It is not heated directly by the flame, but is surrounded by hot gases.

At the top there are necks for the acid vapour, for charging the nitrate, for letting in air, for a thermometer (in a pipe closed at the bottom), and for introducing sulphuric acid. The 8-inch wide neck which carries away the acid vapours is continued into a glass cylinder, through which the inside can be observed, then into an earthenware bend, connected with an earthenware worm of  $2\frac{1}{4}$ -inch bore and 50 square feet cooling-surface, ending in a three-way cock. Then follow two earthenware receivers of 60 gallons capacity each, with outlet-cocks at the bottom, a receiver of 18 gallons, a smaller earthenware worm ( $2\frac{1}{4}$ -inch bore and 25 square feet cooling-surface), a 60-gallon receiver and five 18-gallon receivers, all of them provided with outlet-cocks at the bottom and air-cocks at the top. The second small receiver behind the second worm is charged with water, the fourth with sulphuric acid; in these the inlet-pipes are deep enough to dip into the liquid. The last receiver is connected with the air-pump. The two large receivers behind the first worm receive most of the condensed acid and are alternately put into series by means of the three-way cock; thus the acid can be drawn off without interrupting the work. The joints are all made by means of flanges provided with rills and a cement made of silicate of soda and asbestos. The vacuum helps to keep the joints tight, and they stand very well.

When the nitrate has been charged, all necks are closed, the air-pump is started, and by opening a tap in the connecting-pipe sulphuric acid is drawn in from a store-tank. Much gas is given off at once; first of all nitrosyl chloride, which mostly travels as far as the receivers behind the second worm. When the vacuum has gone up to 500 millimetres of mercury, the fire is started and the thermometer rises to  $80^{\circ}$ , which temperature is kept up during the principal phase. The vacuum is kept at 650 or 670 millim. In the end the temperature must be raised to  $120^{\circ}$  or at most  $130^{\circ}$ . When no more acid distils over, the air-pump is stopped, and the temperature is raised to  $170^{\circ}$  or  $175^{\circ}$ , in order to render the nitre-cake more liquid.

Through this low temperature the decomposition of the nitric acid and the reducing-action of the iron is reduced to a minimum. Therefore the yield is almost equal to theory, and that mostly in the shape of strong acid. With undried nitre and sulphuric acid of  $142^{\circ}$  Tw. the yield is 95.7 per cent. of the theoretical,

in the shape of acid of  $90\frac{1}{2}^{\circ}$  Tw. (78 per cent.  $\text{HNO}_3$ ), and 3.8 per cent. impure acid of  $21\frac{1}{2}^{\circ}$  Tw., together 99.5 per cent. With undried nitre and sulphuric acid of  $160^{\circ}$  Tw. the yield is 99 per cent. nitric acid  $93\frac{1}{2}^{\circ}$  Tw. (81 per cent.  $\text{HNO}_3$ ), and 0.8 per cent. as dilute acid, together 99.8 per cent. The weak acid is left in the receivers till it has risen to  $66^{\circ}$  Tw. With dry nitre and sulphuric acid  $168^{\circ}$  Tw., real nitric monohydrate can be obtained. The usual strength,  $100^{\circ}$  Tw., contains only 0.04 per cent.  $\text{N}_2\text{O}_5$  and no chlorine at all, against 0.95 to 1.92 per cent.  $\text{N}_2\text{O}_5$  in the ordinary  $100^{\circ}$  acid.

While in other processes charges of 6 to 8 cwt. nitre require from 15 to 20 hours to be worked off, here a 16 cwt. charge takes only 7 or 8 hours, and two charges are easily made in 24 hours, which means four or five times the usual quantity. The consumption of coal is 8 or 9 parts for firing and 6 or 7 parts for the vacuum, together 14 or 16 parts to 100 nitre, against 32 to 35 parts in the old process. There is also no steam or compressed air needed for refining the acid. The durability of the retorts is greater than in the old process, and the earthenware vessels do not suffer at all. The temperature of the first receivers is only  $35^{\circ}$  to  $42^{\circ}$ , the back receivers are cold; they never crack, nor do they collapse through the atmospheric pressure, as they are made rather thick-walled and nearly globular in shape. Any cracks in the pipes or bad places in the receivers are cured by putting on asbestos paper soaked in silicate of soda solution. If too much frothing is observed through the glass cylinder, this is at once remedied by opening the air-cock. The total length of the apparatus is only 40 feet, the width of the furnace 17 feet, that of the condensing-plant 5 feet. Large apparatus holding from 50 to 60 cwt. is to be constructed. The sanitary drawbacks of the ordinary nitric acid manufacture vanish when working with a vacuum [how about the action on the air-pump?].

Vogt (Engl. pat. 22018, 1891) manufactures nitric acid by heating an alkaline nitrate with its own weight of an "inert" substance, as lime, oxide of iron, or manganese. The materials are mixed with water into a paste, dried, broken into pieces, and charged into vertical clay or iron retorts heated to  $350^{\circ}$ , while passing through a current of steam and carbonic acid, also heated to  $350^{\circ}$ . Nitric acid distils off and alkaline carbonate remains behind, and is separated from the inert material by

lixiviation. In order to avoid the condensation of lower nitrogen oxides, a little heated air is mixed with the gases issuing from the retort, or previously with the steam and carbonic acid.

Compare also the process of Lunge and Lyte, Engl. pat. 13654 and 13655, 1893 (p. 258), in which ferric oxide is employed and caustic soda is obtained, also that of Garroway, p. 257.

Campbell and Walker (Engl. pat. 9782, 1894) grind nitre-cake (acid sodium sulphate) with nitrate of soda and charge the mixture into retorts provided with a mechanical agitator.

Garroway (Engl. pat. 2466, 1895) prepares nitric acid by heating a mixture of nitrate of soda and copperas or alum, obtaining sulphate of soda and oxide of iron or alumina.

Volney (Journ. Amer. Chem. Soc. 1891, xiii. p. 246) shows that the frothing in the ordinary nitric-acid process takes place only in the last stage, when the strong acid has passed over and when the last portion of the nitre is suddenly acted upon, with formation of weaker acid.

Darling and Forrest (Engl. pat. 5808, 1894) propose obtaining nitric acid by the electrolysis of fused alkaline nitrates, together with metallic potassium or sodium. Patent No. 13171, 1895, extends this process to the production of nitrous fumes (together with sodium oxide) for the manufacture of sulphuric acid.

Siemens and Halske (Germ. pat. appl. S. 8134, 1894) suggest utilizing the well-known formation of nitric acid by the direct union of oxygen and nitrogen under the influence of the silent electrical discharge. This reaction, which under ordinary circumstances is much too slow, is to be promoted by adding ammonia-gas, which causes an abundant formation and separation of solid ammonium nitrate.

Vol. I. p. 96. *Utilization of waste acids from nitrating processes.*—The waste acids from the manufacture of explosives contain much more nitric acid than those from the manufacture of nitrobenzene. Nitroglycerin waste acid contains about 10 per cent.  $\text{HNO}_3$ , 70  $\text{H}_2\text{SO}_4$ , 20  $\text{H}_2\text{O}$ ; gun-cotton acid 11 or 12  $\text{HNO}_3$ , 80  $\text{H}_2\text{SO}_4$ , 8  $\text{H}_2\text{O}$ . These acids, if it is not possible to consume them in a Glover tower, can be used for replacing part of the sulphuric acid in the nitric-acid manufacture; or else they are denitrated by steam, producing sulphuric acid of about 120° Tw. (which is concentrated by evaporation and used over again) and nitric acid, together with lower nitrogen oxides. By passing the



vapours mixed with air through some receivers and then through a "Lunge tower," the nitrogen oxides are also converted into nitric acid, the total being recovered as nitric acid of 70° or even 89° Tw.

A detailed description of the denitrating process is found in O. Guttman's 'Manufacture of Explosives' (London, 1895), vol. ii. p. 177.

*Concentration of Nitric Acid.*—Colin (French pat. 211045) prepares fuming nitric acid of spec. grav. 1·5 by distilling acid of 1·4 with sulphuric acid of 1·84 in enamelled cast-iron retorts, and employing a glass three-way cock for separating the distillates [this apparatus is not practicable].

Erouard (Germ. pat. 62714) also concentrates dilute nitric acid, or waste acids from nitrating processes, by adding strong sulphuric acid, or a solution of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  [!], and distilling the mixture in a vessel in which it travels in a zigzag direction.

H. A. Frasch (Germ. pat. applic. F. 6829, 1893) prepares highly concentrated nitric acid by passing the vapours from the nitric-acid retort through a tower heated above the boiling-point of the acid, in which hot concentrated sulphuric acid is descending, or in which other dehydrating substances, such as anhydrous sulphate of soda or burnt plaster-of-Paris, act upon the mixed vapours.

*Pumping of Nitric Acid.*—For this purpose Paul Kestner, of Lille, has constructed special pulsometers entirely of stoneware, which are supplied by Ludwig Rohrmann, of Krauschwitz near Muskau (Silesia).

Vol. I. p. 96 and Vol. II. p. 122. *Utilization of Nitre-cake.*—Giles, Roberts, and Boake (Engl. pat. 11979, 1890) convert ordinary nitre-cake by addition of sulphuric acid into "pentasulphate,"  $\text{Na}_2\text{O}$ , 5  $\text{SO}_3$ , 3  $\text{H}_2\text{O}$ , which can be packed in iron drums [?] or ordinary casks and usefully employed for certain purposes.

Vol. I. p. 97. *The specific heat of liquid Sulphur Dioxide* has been ascertained by Mathias, Compt. rend. cxix. p. 404. Between  $-20^\circ$  and  $+130^\circ$  C. it is :

$$0\cdot31712 + 0\cdot0003507t + 0\cdot000006762t^2.$$

Vol. I. p. 101. *Injurious action of Sulphur Dioxide upon health.*—Lehmann (Zsch. f. angew. Ch. 1893, p. 612) shows that persons not habituated to sulphurous acid are very little affected by 0·012 pro mille, but perceptibly so by 0·012 pro mille  $\text{SO}_2$ . The

presence of 0.030 pro mille after a few minutes causes strong irritation of the nasal membranes, sneezing, and slight coughing, which symptoms decrease after 10 minutes. The employés and workmen accustomed to it are but little affected by 0.037 pro mille; the sensibility to  $\text{SO}_2$  seems to be lessened by habitually respiring air containing it.

Vol. I. p. 133. *Freezing-points of Sulphuric Acid*.—Thilo (Journ. Soc. Chem. Ind. 1893, p. 827) gives very extended tables as to the results obtained by him in R. Pictet's laboratory. Pictet, himself, subsequently (Compt. rend. cxix. p. 642) supplies the following table:—

Formula.	$\text{SO}_4\text{H}_2$ per cent.	Spec. Grav.	Freezing- point.	Formula.	$\text{SO}_4\text{H}_2$ per cent.	Spec. Grav.	Freezing- point.
$\text{H}_2\text{SO}_4$	100.00	1.842	+ 10°	$\text{H}_2\text{SO}_4 + 15 \text{H}_2\text{O}$	26.63	1.196	— 34°
" + $\text{H}_2\text{O}$	84.48	1.777	+ 3	" 16 "	25.39	1.187	— 26.5
" 2 $\text{H}_2\text{O}$	73.08	1.650	— 70	" 18 "	23.22	1.170	— 19
" 4 "	57.65	1.476	— 40	" 20 "	21.40	1.157	— 17
" 6 "	47.57	1.376	— 50	" 25 "	17.88	1.129	— 8.5
" 8 "	40.50	1.311	— 65	" 50 "	9.82	1.067	— 3.5
" 10 "	35.25	1.268	— 88	" 75 "	6.77	1.045	0
" 11 "	33.11	1.249	— 75	" 100 "	5.16	1.032	+ 2.5
" 12 "	31.21	1.233	— 55	" 300 "	1.78	1.007	+ 4.5
" 13 "	29.52	1.219	— 45	" 1000 "	0.54	1.001	+ 0.5
" 14 "	28.00	1.207	— 40				

Vol. I. pp. 144 and 892. *Action of Sulphuric Acid on lead*.—The extensive investigation made by myself together with E. Schmid, has been published in Zsch. f. angew. Chem. 1892, p. 642, also partly in Journ. Soc. Chem. Ind. 1893, p. 146. I here give a very brief synopsis of our results, some of which are of great practical importance.

1. *In the presence of heat* the purest lead in all cases resists both pure and nitrous sulphuric acid, with or without access of air, much better than "regulus metal" (82 Pb, 18 Sb) or "hard lead" (1.8 per cent. Sb), or even soft lead with only 0.2 per cent. Sb. *In the cold*, lead with 0.2 per cent. Sb is very slightly superior to the purest lead; regulus metal behaves much worse, and hard lead worst of all.

2. *Concentrated nitrous vitriol* is always more active than pure acid. In the case of somewhat dilute acid (spec. grav. 1.72 to 1.76), nitrous vitriol acts less than pure acid on soft lead and hard lead, owing to a protective coating of lead sulphate being formed.

If more dilute, the action is again stronger (comp. below). In all cases nitrous vitriol acts more in the presence than in the absence of air.

3. Comparing two samples of soft lead, the purer sample was found decidedly better; even a very slight proportion of bismuth (0.044 per cent.) acts injuriously.

4. It is altogether inadmissible to judge of the resistance of lead to sulphuric acid from the quantity of the *gas* (hydrogen) evolved. Soft lead gives off at the ordinary temperature, after a week's contact, much gas; hard lead, although losing much more weight, very little gas ( $\frac{1}{20}$  of the theoretical quantity), probably owing to galvanic action. But, on this account, if sulphuric acid is to be sent out in tightly-closed or soldered-up leaden boxes, they should not be made of soft, but of hard lead, since otherwise the hydrogen may bubble up or burst the vessels.

5 (a). Lead containing up to 0.2 per cent. *copper* (alloys containing more copper cannot be homogeneously rolled) is *in the cold* acted upon by strong sulphuric acid more than pure lead; with nitrous acid, there is not much difference. At 100° C. all kinds of acid act in the same way on pure lead and on lead containing copper; concentrated pure acid rather less than concentrated nitrous vitriol, but more than nitrous vitriol of spec. grav. 1.72 (comp. No. 2). At 200° C., concentrated acid acts alike on pure lead and on lead containing 0.02 per cent. Cu; lead containing more copper is slightly less acted upon by pure acid, but rather more by nitrous vitriol.

(b) Above 200° (225° to 255°) lead alloyed with 1 per cent. antimony is far more strongly acted upon than pure lead (in the proportion of 26.5 to 1 at 225°); but lead containing 0.2 per cent. copper resists the acid at 235° much *better* than pure lead in the proportion of 1 : 17, and at 255° in the proportion of 1 : 26.5.

6 (a). Pure soft lead gives no visible evolution of gas with pure concentrated sulphuric acid up to 220°. From this point more and more gas-bubbles are given off, and at 260° the lead is momentarily dissolved with strong frothing, smell of SO<sub>2</sub>, and precipitation of sulphur, the temperature rising to 275°.

(b) The same lead, alloyed with 0.2 per cent. of copper, shows a visible evolution of gas only at 260°, regularly increasing up to the boiling-point (310°), at which the lead is very gradually dissolved.

(c) The lead tested (*sub* No. 7a), alloyed with 1 per cent. Sb,

gives with sulphuric acid the first visible gas at  $175^{\circ}$ , more strongly at  $225^{\circ}$ , and between  $275^{\circ}$  and  $280^{\circ}$  there is the same turbulent, sudden solution as in the case of pure, soft lead. [Bauer, Berl. Ber. 1875, p. 210, found similar results; according to him 0.73 per cent. *bismuth* lowers the temperature of sudden decomposition from  $240^{\circ}$  to  $160^{\circ}$ .]

Hence the purest lead is subject to instantaneous solution by sulphuric acid at  $260^{\circ}$ . An addition of 1 per cent. Sb raises this temperature only about  $20^{\circ}$ , but 0.2 per cent. Cu completely destroys this liability to sudden decomposition.

7. The percentage of *oxygen* in lead is very slight even in extreme cases, and does not seem to have any connection with its liability to be acted upon by acids. But the latter, as may be imagined, is less when the *density of the surface* is *mechanically* increased.

8. The final considerations in selecting the kind of lead best suited for constructing apparatus for the manufacture of sulphuric acid are as follows:—

*For vitriol chambers, towers, tanks, pipes, and all other cases where the temperature can rise but moderately, and certainly never up to  $200^{\circ}$  C., the purest soft lead is preferable to every other description of lead, being least acted upon by hot acid, whether dilute or concentrated, pure or nitrous.*

Any sensible proportion of *antimony* is in nearly all cases *injurious*; *copper* causes at least no improvement. This, of course, does not apply to those cases where the lead requires an addition to its tensile strength, nor to the case mentioned *sub* No. 4 of packages for acid to be closed air-tight. Hence an addition of about 0.2 per cent. antimony may be useful in the case of apparatus which is only in contact with *cold* acid; but with *warm* acid even this percentage is to be avoided.

For *very high temperatures*, *e. g.*, the *hottest boiling-down pans*, which ought not to be heated above  $200^{\circ}$  C., but may sometimes be raised to that point, *an addition of 0.1 to 0.2 per cent. copper is advantageous*, while antimony should be avoided here under all circumstances (*comp. No. 6 b*). That percentage of copper has no action at  $200^{\circ}$ , but only above  $220^{\circ}$ ; and in the presence of bismuth it protects the lead from the sudden destruction sometimes observed.

9. Technical "*sulphuric monohydrate*" at  $50^{\circ}$  C. *acts far more*

*strongly on lead than concentrated sulphuric acid.* [The "monohydrate" employed in our experiments had attracted a little water and tested only 98·85 per cent.  $\text{H}_2\text{SO}_4$ : its action upon lead was  $13\frac{1}{2}$  times that of ordinary concentrated acid of 96·5 per cent.  $\text{H}_2\text{SO}_4$ . Fresh monohydrate of 99·5 or 99·75 per cent. would, no doubt, have shown even more action.]

10. *Nordhausen fuming oil of vitriol* acts upon lead much more strongly than ordinary concentrated acid. When it contains 20 per cent. free  $\text{SO}_3$  it has 32 times the effect of ordinary acid; stronger Nordhausen acid rather less than the 20 per cent. acid, because a protective coat of lead sulphate is formed. At all events lead must not be brought into contact with Nordhausen acid.

11. *Nitric acid* of spec. grav. 1·37 to 1·42 may be bought into contact with lead *at the ordinary temperature*, but no acid of less strength. Stronger acid than the above acts more powerfully upon lead, but no more than concentrated sulphuric acid. *Mixtures of concentrated sulphuric acid and strong nitric acid* act very little indeed upon lead, much less than either strong sulphuric acid or strong nitric acid by themselves: such mixture can be treated in lead vessels without any hesitation.

12. Mixtures of *sulphuric acid and nitrosyl-sulphuric acid*, partly also containing *nitric acid*, all of them originally containing 0·1 per cent. N, but by heating to 65° C. brought to the state in which they can really exist in vitriol chambers, give the following results (entirely agreeing with my former investigations, Vol. I. p. 145):—If a little nitric acid is added to dilute sulphuric acid, and the mixture is heated, a little  $\text{HNO}_3$  is volatilized, but no nitrosyl-sulphuric acid is formed until the concentration has reached spec. grav. 1·5. From this point oxygen escapes, and at spec. grav. 1·768 the whole of the  $\text{HNO}_3$  has vanished,  $\text{SO}_3\text{NH}$  appearing in its stead. Inversely, nitric acid is formed from nitrous sulphuric acid on diluting it; in the case of prolonged heating, this evidently takes place not by splitting up into  $\text{HNO}_3$  and NO, but by absorption of oxygen from the air.

*The action of the acid on lead* is least just about the lowest point where the nitrosyl-sulphuric acid is still capable of existing. It increases with its dilution, and in proportion to this, evidently through the formation of nitric acid, equally with its concentration, and later on rapidly so, the action of stronger sulphuric acid combining with that of nitrosyl-sulphuric acid and nitric acid.

*The minimum action is between spec. grav. 1·5 and 1·6—that is, just at that concentration above or below which the acid ought not to be kept in vitriol-chambers.* This proves that it is not rational to keep the acid in the first chamber too strong (Vol. I. p. 454 *et seq.*).

Vol. I. pp. 164 and 898. *Methyl-orange as indicator.*—It is true that methyl-orange is destroyed by nitrous acid. Nevertheless it can be easily employed in titrating sulphuric or nitric acid containing nitrous acid in two ways: either by adding the indicator shortly before the saturation is completed and quickly finishing the titration, or by supersaturating the acid with caustic soda and retitrating with standard acid.

Nitrous acid acts upon methyl-orange like a strong mineral acid, and is therefore completely saturated before the pink colour has changed to yellow, if there is not time for the colouring-matter to be destroyed.

Vol. I. p. 170. *Reactions on nitrogen acids in Sulphuric Acid.*—As I have shown in Zsch. f. angew. Chem. 1894, p. 345, the diphenylamine reaction is best employed in the following manner: 0·5 gram white diphenylamine is dissolved in 100 c. c. pure strong sulphuric acid, adding 20 c. c. water; the heat assists in dissolving the substance, and the reagent keeps in well-stoppered bottles a long time without turning brown. When testing for nitrogen acids, pour a few c. c. of the specifically heavier liquid into a test-tube, and carefully pour the specifically lighter liquid on the top, so that the layers only gradually mix. The presence of as little as  $\frac{1}{10}$  milligram nitrogen in the shape of nitrogen acids per litre is indicated by a blue ring forming at the surface of contact of both liquids, most easily perceived by holding the glass sideways against a white background. Both nitric and nitrous acid are indicated in this way.

Contrary to the opinion formerly held, I have shown that *brucine* indicates only nitric acid, which can thus be proved to exist in the presence of nitrous acid. It is, however, necessary to have a great excess of sulphuric acid. The reagent is best prepared by dissolving 0·2 gram brucine in 100 c. c. pure strong sulphuric acid. 1 c. c. is added to 50 c. c. of the liquid to be tested, of which at least three-fourths must consist of strong sulphuric acid. If as little as  $\frac{1}{100}$  milligram nitrogen is present in the shape of nitric acid, a pink colour is produced, which gradually passes through orange into yellow, more quickly when heating.

I have shown, *loc. cit.*, how this can be utilized for colorimetrically estimating very slight quantities of nitric acid. *Selenium* has no action on brucine; somewhat larger quantities of ferric salts render the reagent less sensitive.

Vol. I. p. 177. *Colorimetric estimation of slight quantities of Nitrous Acid.*—As I have shown in Zsch. f. angew. Ch. 1894, p. 348, this can be performed by Griess's reagent, as modified by myself and prepared as follows:—0.1 gram white  $\alpha$ -naphthylamine is dissolved by boiling in 100 c. c. water for a quarter of an hour; then 5 c. c. glacial acetic acid (or its equivalent in ordinary acetic acid), and a solution of 1 gram sulphanilic acid in 100 c. c. water are added. The solution is kept in a well-stoppered bottle; if it turns pink it is decolorized by shaking with zinc-dust and filtering. A very slight colour does not interfere with its use, as only 1 c. c. is employed for 50 c. c. of the solution to be tested. 1 c. c. of the reagent indicates  $\frac{1}{1000}$  milligram nitrite-nitrogen in 100 c. c. water by turning the water pink in 10 minutes. Strong mineral acids retard or stop the reaction, but this can be remedied by adding a large excess of pure sodium acetate.

For quantitative use I prepare a standard solution as follows:—0.0493 gram pure sodium nitrite, containing 0.010 gram nitrogen, is dissolved in 100 c. c. water, and 10 c. c. of this solution is mixed with 90 c. c. pure sulphuric acid; the resulting mixture contains  $\frac{1}{100}$  milligram of nitrite-nitrogen in a perfectly stable form. Two colorimeter cylinders are charged as follows:—Each of them receives 1 c. c. of the Griess-Lunge reagent, 40 c. c. of water, and about 5 grams of solid sodium acetate. To one of these is added 1 c. c. of the standard solution, to the other 1 c. c. of the acid to be tested. The contents of each cylinder are at once thoroughly mixed, and after 5 or 10 minutes the colours are compared. If they are not equal, the more strongly coloured liquid is diluted up to the point where layers of equal thickness show the same depth of colour in both solutions, and the per-centage of nitrite-nitrogen is calculated from the amount of dilution.

Vol. I. p. 205. *Brimstone-burners.*—Fish (Engl. pat. 7757, 1891) provides the burner with a bed inclined to one side, so that the sulphur is gradually moved forward to that side, and the ashes can be raked out of a receptacle provided for the purpose.

Vol. I. p. 220. *Grate-bars for pyrites-burners.*—Dr. Burgemeister (private communication) employs bars made of a cruciform section.

When turning these round, the smaller pieces easily fall through ; the larger lumps get between the bars and either pass through on turning back or are crushed. The following diagram shows the different positions of the bars :

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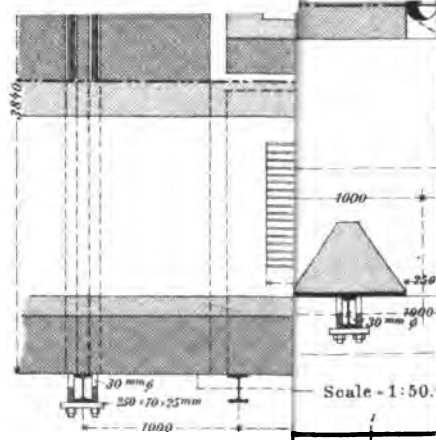
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Vol. I. p. 229. *Burners for roasting copper-matte*.—Hæge (Berg- u. Hüttenm. Zeit. 1893, p. 383) describes the process introduced by him at Britonferry, near Swansea. The copper-matte produced there could not be roasted in Mansfeld kilns, nor in ordinary pyrites-burners. The desired result was obtained by increasing the heat, in the first instance by a suitable treatment of the matte, and in addition to this by improving the construction of the burners. The matte was rendered porous by tapping it on to a sand-bed slightly moistened and dusted over with fine coal. It was then crushed by a Blake's stone-breaker, in which one of the corrugated faces had been substituted for a smooth one, so that flat, more tightly lying pieces were obtained, which were separated from the smalls by a riddle with meshes of  $\frac{3}{8}$  inch width. The burners are of the ordinary shape of English pyrites-burners, described in the text of this book, but of slightly different dimensions :—Grate surface 4 ft. 3 in. by 4 ft. 4 in.; area at the level of the upper working-surface 5 ft. by 4 ft. 9 in.; height from grate-bars to the upper working-surface 2 ft., to spring of the arch 3 ft. 4 in., to the crown of the arch 3 ft. 8 in.; smoke-flue at the lowest point 6 in., at the highest 1 ft. 4 in.; total outside height 7 ft. 10 in. The heating-up takes place from the top, exactly as described in the text; the burners are ready for work in two or three days. Each burner then receives a charge of from 6 to 7½ cwt. of crude matte every 12 hours. After three hours everything becomes red hot, after six hours a bright cherry-red heat is attained. Now the interior of the burner is worked up through the middle door by means of a steel poker, 2½ in. thick, pointed at one end; any lumps formed are broken up; and this working over is continued through the upper door. After another two or four hours the heat is at its maximum; the upper working-door is now mostly at a dark-red heat. Then the heat decreases; 11½ hours after charging the grate-bars are turned and shaken, in order to remove the roasted matte, and after 12 hours a new charge is made. There is no picking out and







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recharging of imperfectly roasted matte, since everything is well finished. The draught must be well regulated; there should be a slight plus-pressure within the burner. In this way mattes containing from 20 to 47 per cent. copper are treated. The poorer matte yields rather hotter and richer gas and more sulphuric acid than the richer. With 20-per-cent. matte the roasted product contains 9 per cent. sulphur, with rich matte it contains 11 per cent. sulphur; both are at once ready for the concentrating work. From 40 per cent. matte about 47 or 48 per cent. of the weight of roasted matte is obtained in the shape of chamber acid of 110° Tw., with consumption of 0.8 to 1.0 nitre per cent. of chamber acid. The gases are hot enough to thoroughly decompose the mixture of nitre and sulphuric acid in the nitre-oven and to denitrate the acid in the Glover tower; the acid flows from this with a temperature of 140° to 155° C.

Vol. I. p. 260. *MacDougall's mechanical pyrites-burners* have been further improved by pat. No. 22504, 1891. The central shaft is now made in several lengths, coupled together by widening one end of the shaft to form a square socket, and fitting into this the square end of the other shaft, the two secured by a square key wedged between socket and square end; a tight-fitting spring-clip protects the coupling from the action of the burner-gas. The furnace rings are joined together by half check-joints secured by set pans and rust jointing; the ends of the pins are not exposed to the corrosive fumes.

*Other mechanical burners.*—As stated in Zsch. f. angew. Ch. 1894, p. 134, I have met with several Spence furnaces at work in America, but they did not give general satisfaction. A Johnson furnace was commended as superior. Excellent results have been obtained with the mechanical furnace of H. Frasch, described *ead. loco*, p. 15, which is very similar to MacDougall's, but is provided with internal water-cooling of the shaft and agitating-arms, and thus avoids the ordinary drawbacks of such mechanical furnaces.

Vol. I. p. 275. *Roasting of zinc-blende.*—Figs. 227 to 230 show a blende-roasting furnace, as constructed at the Rhenania Chemical Works at Stolberg, which have been found to perform the work in excellent style. These furnaces require two men per shift, and roast about 4 tons blende per 24 hours, with a consumption of 16 cwt. of coal. The temperature of the top muffle is 580° to 690°,

that of the following muffles 750° to 900°. The progress of roasting is shown by the following percentages of sulphur :—

Raw ore.....	19.2	26.8		26.5
End of first muffle .....	17.6	19.1	to 21.9	15.9 to 21.4
„ second „ .....	12.0	11.2	„ 14.3	9.9 „ 12.4
„ third „ .....	3.4	1.02	„ 1.48	0.75 „ 1.06
„ roasting .....	0.6	0.35	„ 1.02	—

In the case of richer ores the second muffle does not require heating; the fire-gases may be conducted below the third muffle without a partition, and then at once over the second roasting-bed.

Jahne (Zsch. f. angew. Ch. 1894, p. 305) describes some experiments made with these furnaces. They are greatly improved by arranging a partition cutting vertically through all three muffles and thus dividing the furnace into two parts, without any change in the firing. This admits of roasting 30 per cent. more ore down to the same percentage of sulphur and saves labour. It is best to build two furnaces back to back. On the top beds the ore is spread in layers twice as thick as on the bottom beds, leaving small gaps between the charges, to prevent their getting mixed. It takes three or four days before a batch charged at the top is discharged at the bottom. The raking over and moving on of the batches, following upon the discharging of a finished batch, requires 4 hours. The most careful work must be bestowed upon the finishing of the batches in the hottest place; this lasts at best  $1\frac{1}{2}$  hours, usually 3 to 4 hours, sometimes 7 to 8 hours. Tests are made by adding hydrochloric acid to a sample, and looking for any evolution of  $H_2S$ . The sulphur can be brought down to 0.1 or 0.2 per cent.; it ought never to exceed 1 per cent., except in the case of blends containing limestone, which may retain 2 or 3 per cent. S in the shape of calcium sulphate. In regular work a charge of 9 to 12 cwt. roasted ore is drawn every 6 hours. 100 parts of raw blende average 85 of roasted ore, and require 25 or 26 parts of good coal. The furnaces are provided with large dust-chambers, which must be cleaned every few weeks. The dust consists mainly of zinc sulphate and calcium sulphate. Lead oxide is carried farthest, even through the ten cylinders of a Hargreaves plant connected with the furnace at Stolberg, right into the earthenware receivers of the acid-condensing plant. If the blende contains mercury, that metal is found in the mud of

the vitriol-chambers connected with blende-furnaces, and can be recovered from it by distillation.

Bémelmans (Germ. pat. 76775) describes a furnace for roasting both pyrites and blende in separate compartments; the sulphur vapour obtained from pyrites, sometimes by addition of coal, is utilized for removing from the blende (which must not be mixed with coal) arsenic, antimony, and phosphorus in the shape of volatile sulphides.

Jensch (Zsch. f. angew. Chem. 1894, p. 50) shows by analyses that the sulphur in roasted lende is mostly contained therein in the shape of ferrous sulphide; when roasting down to 2 per cent. S, no ZnS is present, and it is therefore quite unnecessary to drive the roasting down to 0.5 per cent. S, as is sometimes demanded.

Vol. I. p. 280 and p. 310. *Production of Sulphur Dioxide for manufacturing Calcium Disulphate (in the manufacture of wood-pulp, &c.).*—In this case the conditions are very different from those mentioned in the text. There is no question of having to provide the oxygen for forming  $\text{H}_2\text{SO}_4$  from  $\text{SO}_2$  and the excess of oxygen practically necessary in the lead chambers; and the formation of  $\text{SO}_2$  in the burners should be avoided as much as possible. The operation should be conducted so as to exceed as little as possible the amount of oxygen demanded by the equation:  $2\text{FeS}_2 + 11\text{O} = \text{Fe}_2\text{O}_3 + 4\text{SO}_2$ , which corresponds to a theoretical maximum of 16 per cent.  $\text{SO}_2$  by volume in the burner-gas. Practically, however, 11 per cent. should not be exceeded, because otherwise the burners get too hot, which causes the sublimation of sulphur and the formation of scoria in the burners. The pyrites should be broken into pieces of not more than  $1\frac{1}{2}$  inches diameter, and all below  $\frac{1}{4}$  inch diameter must be sifted off. For lump ore the ordinary kilns are used, as described in the text. There is no advantage in employing pyrites smalls, as they cannot be burned without admitting more air than is suitable for the purpose in question.

Vol. I. p. 280. *Condensation of acids from smoke-gases, &c.*—Egestorff's Salzwerke (Germ. pat. 70396) arrange in the smoke-flue several chambers in series, with inclined bottoms connected with collecting-wells; in these the gaseous current meets with an alkaline absorbing-liquid, converted into spray by a steam-jet, and subsequently again pumped up and used as a spray.

Bémelmans (Germ. pat. 77335) converts the  $\text{SO}_2$  by reduction with carbon and hydrogen into  $\text{H}_2\text{S}$ , dries this by the process to be described below, mixes it with dry  $\text{SO}_2$ , and converts them into  $\text{H}_2\text{O}$  and  $\text{SO}_3$ .

Vol. I. p. 285. *Rössler's process for forming Cupric Sulphate from copper, air, and sulphur dioxide (in smoke-gases).*—Fries (Chem. Ind. 1895, p. 137) has made a long series of experiments with this process, with totally negative result. No oxidation of  $\text{SO}_2$  with air to  $\text{SO}_3$  by the catalytic action of  $\text{CuSO}_4$  could be proved.  $\text{SO}_2$  reduces a hot solution of  $\text{CuSO}_4$  with intermediary formation of cupric sulphite, to metallic copper. A smooth and easy oxidation of the cupric sulphite to sulphate does not take place. Hence this process would be useless for the production of cupric sulphate, and still more so for that of sulphuric acid. [The latter has been already alluded to in Vol. I. p. 877: but the manufacture of cupric sulphate by that process seems to be proved practicable by experience on the large scale.]

Vol. I. p. 295. *Carriage of liquid Sulphur Dioxide.*—Boake and Roberts (Engl. pat. 19789, 1892) find that liquid  $\text{SO}_2$  does not act on tin or soft solder, and that therefore these can be employed in the manufacture of carrying-vessels.

Soy (Engl. pat. 12276, 1893) patents the process of sending out liquid  $\text{SO}_2$  in glass vessels sealed by the blowpipe, to be broken by a hammer in the rooms to be disinfected.

Vol. I. p. 300. *Dust-chambers for acid-smoke at the Freiberg works.*—Bauer (Jahrb. f. Berg- u. Hüttenm. 1894, p. 39) states that the nine sets of chambers connected with the Freiberg smelting-works (containing 30 lead chambers) possess 8037 metres of flues, of 3·8 square metres section. The flue-dust in 1893 contained 1137 kil. silver, 1656 tons lead, and 917 tons arsenic, of a value of £13,600. Eighty per cent. of the dust is recovered, 20 per cent. has hitherto been lost. The damages to be paid have diminished from £3050 to £180. At present new flues on the Monier-Freudenberg system are built for recovering the last 20 per cent. of dust. The rate of cooling of the gases is  $1^\circ \text{C}$ . per 8·3 metres length in closed-in Monier flues, per 4·5 metres in freely exposed Monier flues, per 3 metres in leaden flues, and per 6 metres in brick flues.

Vol. I. p. 343. *Iron lead-chamber frames.*—I found these to be constructed in the following manner at a factory where they

answered very well. The side-frames consist of thin angle-irons, crossing each other at right angles, the uprights 9 ft. 6 in. and the horizontals 7 feet distant from each other. No iron nails are employed at all; the lead straps are simply bent round the angle-irons. The roof is suspended from angle-irons in exactly the same way.

Vol. I. p. 365. *Dividing vitriol-chambers into sets of several chambers.*—In America (Zsch. f. angew. Chem. 1894, p. 133) I found at one place a set of 12 chambers of equal size, each 24 feet long, which, it was asserted, combined very good yield with small consumption of nitre. At another place they had three chambers, 60, 50, and 40 feet in length, with plate-columns between.

Vol. I. p. 375. *Electrically produced oxygen for feeding vitriol-chambers.*—Scheurer-Kestner (Bull. Soc. Ind. Mulh. 1890, p. 276) calculates the cost of 490 kil. oxygen, corresponding to a metrical ton of sulphuric acid, at 176 frs. = £7, which of course renders the employment of such oxygen entirely out of the question.

Vol. I. p. 375. *Proposals for diminishing the chamber-space.*—Hacker and Gilchrist (Engl. patent 15895, 1893) employ the same principle as I have adopted in my "plate-columns," to which they expressly refer. Instead of my geometrically constructed stoneware plates for dividing the gases, the liquid acid, and the acid vapour, they employ a number of horizontal lead tubes, running from one side of the tower to the other and alternating in position. These towers, which they call "pipe-towers," are fed with water or sulphuric acid; cold air is drawn or blown through the pipes. A paper in Journ. Soc. Chem. Ind. 1894, p. 1142, contains a detailed description of this system, in discussing which several speakers threw much doubt upon the efficiency of this system [a very imperfect imitation of the "plate-columns"!].

Walter and Boeing (Germ. pat. 71908) attempt the diminution of the chamber-space by hollow partitions, made of acid-proof material, arranged across the whole width of the chambers. Double walls are constructed of such a form that the principal gaseous current enters through large holes near the bottom, rises upwards in the space between the walls and issues at the top; at the same time the gases are allowed to penetrate into the inner space by numerous small openings, and to issue in the same way on the other side, so as to produce a good mixture. Buttresses and

binders produce sufficient stability without interfering with the draught, which is also procured by making the sectional area of the openings and joints much larger than that of ordinary connecting-pipes. [This system aims at attaining the same object as plate-columns in a simpler way and without interfering with the draught. But, in consequence of the many outlets offered to the gases, it is doubtful whether they will travel exactly in the desired path. The stability of such inner walls, even when made of the best material, is very doubtful indeed, and a collapse would produce most disastrous results.]

Brulfer (French pat. 220402) also employs hollow brick partitions within the chambers; he adds dividing apparatus, made of lead tubes with air-cooling, fixed behind each partition. When the gases have passed through a cooled divider, they again pass through a hollow brick divider.

Benker (French pat. 238872) places between the chambers leaden towers, 5 feet wide and 20 or 25 feet high, filled with earthenware cylinders 4 inches wide and 3 to 4 inches high. They are fed with nitrous vitriol from the Gay-Lussac towers at the top, and with a steam-jet at the bottom. The strength of the out-flowing acid is maintained between  $112^{\circ}$  and  $123^{\circ}$  Tw.; it is kept a little nitrous, to avoid the reduction going too far. Such a tower is placed behind the first chamber, which is made large enough to consume all the steam coming from the Glover tower; another tower is placed between the second and third chamber.

Dr. Burgemeister (private communication) proposes arranging a number of lead pipes, 15 to 18 inches wide, vertically between top and bottom of the first chamber, and cooling these by air passed through. [This plan will hardly be practicable, as the immense extension of joints, especially at the bottom, will cause too many interruptions for repairs.]

Pratt (Engl. pat. 4856, 1895) places a fan or steam-injector in front of the chamber, and a tower, fed with weak sulphuric acid, at the end of the chamber, the gases issuing from the top of this tower being re-injected into the chamber by means of the fan. Baffling columns may also be placed within the chamber.

Vol. I. p. 381. *Diminution of chamber-space by the application of Lunge and Rohrmann's plate-towers.*—In Zsch. f. angew. Chem. 1895, p. 407, P. W. Hofmann mentions an experiment made in



that direction which failed because the holes in the plates, 8 mill. bore, became filled with liquid and thus stopped the draught. Lunge (ibid. p. 409) completely refutes this objection, mentioning that already about 200 plate-towers are at work, most of them with even smaller holes, and a large number with 8 mill. holes, in sulphuric-acid works. These works have been very successful, as was authentically proved by interrogatories filled up by the respective firms, produced at the meeting in question. These documents also prove that, if the section of the tower is sufficiently large, no trouble is caused by draught of the kind mentioned by Hofmann.

The part played by the Lunge-Rohrmann plate-towers in the manufacture of Sulphuric Acid is discussed at length by Niedenföhr, in 'Chem. Zeit.' 1896, p. 31. I give a short abstract from his paper:—The plate-towers are not very well adapted for replacing the whole of the ordinary vitriol-chambers; the first part of the process is always best carried out in a single lead-chamber, as here the gases are still sufficiently concentrated to react upon each other. [In this view, as well as in all other essential points of Niedenföhr's paper, I fully concur.] Here also the flue-dust and the excessive rise of temperature would act injuriously. Hence it is not advantageous to place a Lunge tower between the Glover tower and the first chamber, but it should be placed in the central or back part of the set of chambers. Even then the results obtained with these towers do and must differ at different works, according to circumstances, viz., the available chamber-space, the draught, the size of the burners and of the connecting-pipes, of the Gay-Lussac tower, and so forth. In some cases the working capability of the tower is partly taken up for correcting some fault in the set of chambers to which it has been applied. Niedenföhr quotes the following special instances of the work done by Lunge towers, as personally observed by him in the cases stated.

In one case, a Lunge tower was placed between the two chambers of a set, which were of equal size; the total length of the set was 193 ft. 6 in. and its contents=94,640 cubic feet. The quantity of Sicilian sulphur burnt previously did not exceed 30 cwt. per 24 hours, but after putting up the tower it could be raised to 46 cwt., evidently because the time and the length of the path of the gases had been thereby increased to such an extent that the set could be

worked with stronger draught, and more sulphur could be burnt accordingly. In another case (4 chambers, total capacity 38,150 cubic feet, length 78 ft. 6 in.) the production could be increased from 15 to 18 cwt. of Sicilian sulphur per day. This means that some improvement had been effected, but principally in this respect, that the previously observed fault, viz. the carrying forward of the process into the Gay-Lussac, was now avoided. In a similar case, the production rose from 16 to 19 cwt. of sulphur; in both cases less nitre was consumed than previously. The towers thus spent part of their efficiency in correcting the faults of the old plant, and this in many cases would be a very desirable object, but the quantitative results thus obtained do not represent the whole of the working capacity of the towers, which in some more favourable cases has admitted of increasing the production by 45 per cent. Nearly in every case observed by Niedenführ, this capacity of the towers had not been exhausted, for the chamber following upon the towers had hardly any more work to do; more work could have been done by increasing the number of the burners, by enlarging the connecting-pipes, or by other suitable measures. The very low temperature of the back-chambers in this case, however, is useful in condensing part of the nitrous gases and lightening the work of the Gay-Lussac tower. Formerly the acid from the Lunge towers was sometimes too nitrous, but this drawback has been avoided by feeding the towers with acid of from 38° to 42° Bé. (spec. grav. 1.357 to 1.410).

The Lunge tower cannot be simply substituted for a Glover tower, as the holes of the plates would be too quickly stopped up by flue-dust, and in washing this down they would easily crack. Niedenführ, however, recommends placing a few tiers of plates with  $\frac{1}{2}$ -inch holes in the upper part of the tower. He quotes a case where a Lunge tower was found specially useful in completely denitrating chamber-acid required to be entirely free from nitrogen compounds. [Comp. another case of special usefulness, *infra*, p. 785.]

Especially good results have been obtained in a number of cases, personally observed by Niedenführ, where plate-towers were employed as auxiliaries to Gay-Lussac towers. They act not merely in promoting the absorption of the nitrous gases, but also in rendering the chamber-work much more regular, especially in

places where the chambers are subjected to sudden changes of weather, gales, &c.

Although all the data for planning a sulphuric-acid plant are not yet known, including the employment of plate-towers, with absolute certainty as to the quantitative results, yet Niedenführ believes that the following plan is most likely to answer its purpose. Instead of an ordinary lead-chamber plant, of a capacity of 106,000 cubic feet, the following apparatus should be employed:—The gases coming from the Glover tower pass through a pipe 3 ft. wide into the first chamber, 23 ft. wide, 20 ft. high, 40 ft. long, where the first and most intense reaction takes place. They issue through a 2 ft. 6 in. pipe into a plate-tower, consisting of 10 or 12 layers of 12 plates each; from here they pass into the second chamber,  $16\frac{1}{2} \times 20 \times 23$  ft.; from this by a pipe of 2 ft.  $4\frac{1}{2}$  in. diameter into a second plate-tower, consisting of 16 layers of 9 or 10 plates. They now travel through a 2 ft. 3 in. pipe into the third chamber, of the same size as the first. They are then carried through a long pipe (say 80 ft.) of 2 ft.  $1\frac{1}{2}$  in. diameter into a plate-tower, consisting of 18 or 20 layers of 8 or 9 plates each, which serves as first Gay-Lussac tower, and is followed by an ordinary coke-filled Gay-Lussac, 26 ft. high. The dimensions of pipes and towers have been chosen so as to produce a uniform velocity in the pipes and a retardation of draught in the plate-columns. If the final draught is not sufficient, the exit-pipe from the Gay-Lussac may be provided with a Körting's antimony-lead blast.

Vol. I. p. 404. *Nitre-ovens.*—Rice (Engl. pat. 16757, 1892) takes out a patent for an arrangement observed in some places as a matter of course for many years past, viz. putting the nitre-oven between the burners and the Glover tower in such manner that, by means of valves, the burner-gas can be made to travel either through the oven or directly into the chambers.

Vol. I. p. 410. *Injector for Nitric Acid.*—Dr. Burgemeister (private communication) employs a platinum nozzle (*not* soldered with gold!) and a steam-jet placed just below, the latter consisting of a platinum nozzle, about  $\frac{1}{8}$  wide, inside the chamber, continued outside into a copper tube. Both tubes pass through a lead pipe burnt into the chamber side, and are cemented in this with glycerine-lead cement.

From other sources I hear that *glass* nozzles are preferable in all cases, more especially also for the water-spray producers replacing steam-jets (Vol. I. p. 421 and p. 424), as all platinum-jets become gradually widened by the jet of water.

Vol. I. p. 425. *Artificial promotion of draught in the vitriol-chambers.*—I have described in the text the various drawbacks connected with the application of injectors for this object ; I have indeed not found such apparatus in the works I have visited during the last few years. But several works have adopted the plan, originally followed at Freiberg, of promoting the draught by fans made of lead alloyed with antimony, or wood covered with lead, fixed on iron axles, running in somewhat tightly fitting lead journals without stuffing-boxes. Such fans are arranged either between the Glover tower and the first chamber, or between the last chamber and the Gay-Lussac tower, or in both places. These fans are worked at a trifling expense, most conveniently by electro-motors, which avoid the necessity of shafting and gearing; and this process should be more frequently employed, not merely in such extreme cases as at the Freiberg works, where the gases must travel through flues of 330 feet length, but in ordinary chambers, which are thus made independent of accidental variations of pressure, of low chimneys, &c.

Fallding has applied such artificial draught for making sulphuric acid in plate-columns alone, without any lead chambers.

Vol. I. p. 482. *Depth of acid in the chambers.*—In the text I have quoted the view generally held by practical men, according to which it is of great importance for the regularity of the chamber work to keep a somewhat deep layer of acid, 8 inches or upwards, at the bottom of the chambers. I have stated as the probable cause of this the fact that this layer serves as regulator for the variations of strength and the percentage of nitre in the acid directly connected therewith. This view is completely confirmed by observations communicated to the 30th Alkali Report, p. 66, by Mr. Carpenter. At a factory where the chamber receives its nitre mostly in the shape of waste acid from the manufacture of nitro-toluol, a film of nitro-toluol is formed on the surface of the chamber-acid, and this shutting-off of the acid from the atmosphere of the chamber causes exactly the same irregularity in the working of the chamber as a low depth

of the acid would have done. The latter no doubt mainly serves as regulator for the nitre.

Vol. I. p. 507. *Calculation of the Sulphur burnt from percentage of oxygen in the exit-gas.*—An erratum occurs in the formula in the last line of this page; instead of  $\frac{1}{1.00367} t$  it should be  $\frac{1}{1.00367} t$ .

Vol. I. p. 519. *Drawbacks of coke-packing in Gay-Lussac towers.*—Hallwell (Chem. Zeit. 1893, p. 263) remarks that in a case observed by him the replacing of coke packing by stoneware packing led to a considerable saving of nitre.

Vol. I. p. 519. *Repacking Gay-Lussac towers.*—As this operation in the case of coke-towers has to be performed from time to time, and accidents have happened through the gases remaining in the tower, official rules have been laid down in Germany, of which the principal points are the following:—Before repacking is commenced, the tower must be completely disconnected from the chambers, but the connection with the chimney must be left open. The tower must now be washed first with sulphuric acid, then with water or steam, until the liquid running off tests at most no more than 3° Bé. (1.022). During the taking-out of the coke there must always be draught into the chimney: when unpacking from below the draught should act from the top; when unpacking from the top the draught should act from the bottom. If this cannot be done, the cover must be removed and a large hole cut in the side at the bottom. Towers packed with coke must be unpacked from the side and from without, in the case of tall towers on different levels. The packing material must be immediately removed. The workmen must be provided with mouth-sponges, respirating-apparatus, india-rubber gloves, &c. Before removing the mud collected at the bottom, it must be stirred up from without with water, and this must be repeated if nitrous vapours are evolved. No men suffering from lung or heart disease are to be employed in this kind of work.

The English Alkali Report, No. 31, p. 90, mentions a fatal accident which occurred in repacking a well-washed and unpacked Gay-Lussac tower, and which was evidently caused by the nitre-gas retained by the old brick-lining. It is therefore recommended to ventilate the towers in all cases from the top downwards during unpacking and repacking.

Fig. 231.

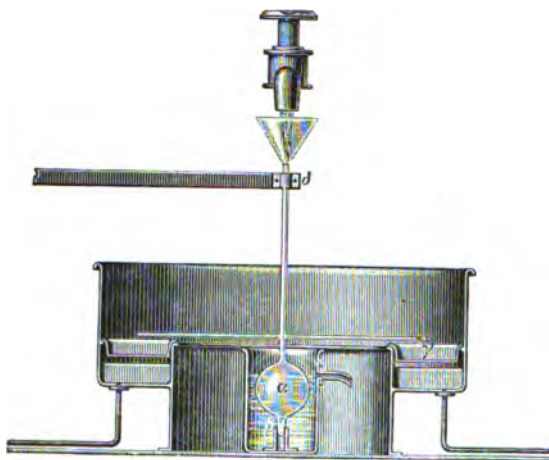


Fig. 232.

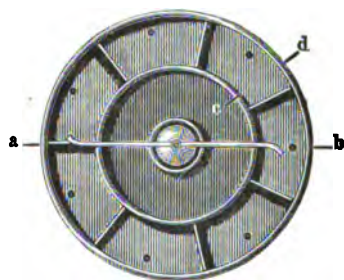


Fig. 233.

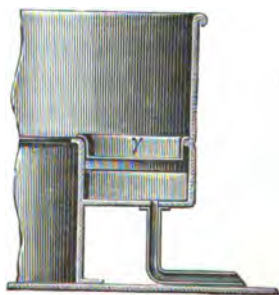
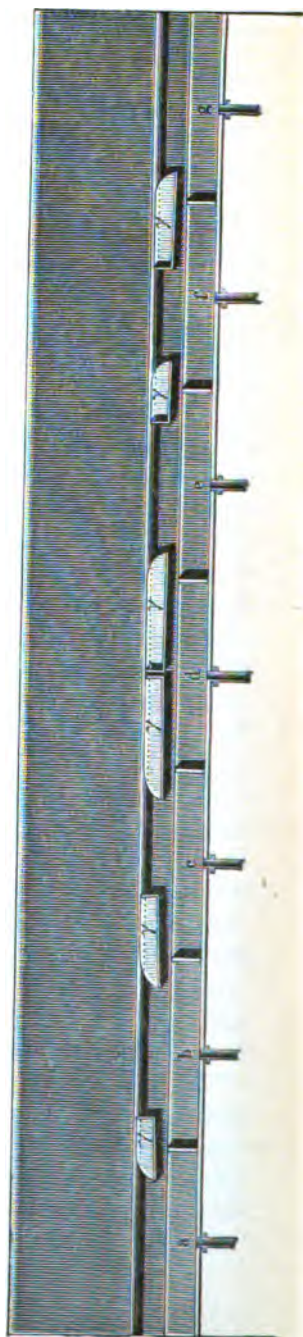


Fig. 234.



Vol. I. p. 534. *Centralized working of the Gay-Lussac towers.*—The following very perfect system is followed at the celebrated Griesheim works. Seven sets of chambers are employed, each possessing ordinary Gay-Lussac towers; the whole of these communicate with a large common tower, of a horizontal section of  $10 \times 30$  ft., which receives the fresh acid of  $142^{\circ}$  Tw., divided into 480 jets. The resistance in this tower amounts to  $1\frac{1}{2}$  up to  $\frac{1}{2}$  in. of water. The weak nitrous vitriol formed here is pumped up and feeds the ordinary Gay-Lussac towers. Since these require variable quantities of acid, this is divided among the seven towers by an acid-wheel possessing seven chambers of variable dimensions, produced by slightly inclined movable spouts resting on the partitions between the chambers. By shifting these spouts backwards or forwards, the time of feed and also the quantity of acid serving each compartment can be varied at will. From each compartment a pipe conducts the acid to one of the Gay-Lussac towers, where it is again subdivided in the ordinary way. (In the same place there is a similar arrangement for dividing the strong nitrous acid, chamber acid, and nitric acid among the seven Glover towers, placed at a considerable distance from the central office.) Figs. 231 to 234 illustrate the above. Fig. 231 shows the acid-wheel, supported by the glass bulb  $\alpha$ , floating in a vessel filled with sulphuric acid. This avoids all friction, so that the wheel never stops. The glass point  $\beta$  and a short piece of tubing at the bottom form one of the guides; a thimble  $\delta$  just below the funnel forms the other guide. We notice the seven compartments  $a, b, c, d, e, f, g$ , and the spouts  $\gamma$ , which can be moved backwards and forwards, and thus admit of dividing the supply at will. Thus, for instance, in fig. 234, which indicates a section through all the seven compartments (projected on a straight line), we find that the acid is divided among the six compartments  $a, b, c, e, f, g$  in the proportion: 7, 7, 7, 8, 5, 8;  $d$  receives nothing, because the set of chambers to which it belongs is standing still.

The employment of Lunge-Rohrmann's *plate-columns* as auxiliary Gay-Lussac towers is mentioned, *supra*, p. 778.

Vol. I. p. 539. *An automatic acid-egg air-valve* is described in Chem. Tr. Journ. xvii. p. 82 (J. Soc. Chem. Ind. 1895, p. 749). The acid entering the egg tends to raise a wooden float, and this lifts a valve connected with the air-tap. When later on the com-

pressed air forces the acid out, the float descends and the air-supply is automatically shut just as the last acid is being driven out.

Vol. I. p. 554. *Temperature in the Gay-Lussac tower.*—Crowder (Journ. Soc. Chem. Ind. 1891, p. 300) doubts the necessity of cooling the acid required for feeding the Gay-Lussac towers, except with the view of its action on the lead, on the strength of laboratory experiments in which acid of spec. grav. 1.75 did not absorb the nitrous vapours from chamber-gases much less at 100° than at the ordinary temperature. But as he never went beyond 0.47 or at most 0.69 per cent.  $N_2O_3$  in the acid, his observations are not to the point. We know from observations made on the nitrous acid tension of sulphuric acid (Vol. I. p. 894) that this increases rapidly with the percentage of  $N_2O_3$ , and in all cases with the rise of the temperature. As regards such low percentages of  $N_2O_3$  as those employed by Crowder, the tension of  $N_2O_3$  is not very great even at higher temperatures; but in actual work we must aim at higher percentages of nitre, in which case any higher temperature of the acid acts injuriously. These remarks, made already in the "Addenda" to Vol. I. p. 902, have been fully confirmed by observations communicated by Hasenclever (Chem. Ind. 1893, p. 337). A high temperature not merely prevents the absorption of  $N_2O_3$ , but even expels it from stronger nitrous vitriol.

Vol. I. p. 559. *Treatment of the exit-gases from the Gay-Lussac towers.*—These gases always contain a little nitric oxide, which escapes oxidation by the excess of air present, in consequence of its great dilution. They are sometimes washed with *water* in a special small coke-tower or plate-column, where a little weak acid is formed, which is taken back to the Glover tower.

Mitarnowski and Benker (French pat. 212989) propose passing these gases through a solution of ferric sulphate, or through a column charged with granulated copper and fed with water.

Vol. I. p. 582. *Composition of Glover-tower bricks,* called "metalline," supplied by the Buckley Brick and Tile Company, according to Chemical Trade Journal, x. p. 46:—63.01  $SiO_2$ , 25.95  $Al_2O_3$ , 6.49  $Fe_2O_3$ , 0.75  $Mn_2O_4$ , 0.83  $CaO$ , 0.40  $MgO$ , trace of  $Na_2O$ , 2.57  $K_2O$ , 0.9 organic substance and water.

Vol. I. p. 582. *Packing Glover towers.*—Knab (Germ. pat. 67085) causes an unimpeded transit of the gases and prevents obstructions by a special kind of packing. He forms in the centre



of the tower a column consisting of superposed cylinders. Each cylinder is provided with six slightly inclined earthenware tubes, arranged star-shape, and with their outer ends reaching into the brick lining of the tower. These stars are alternately arranged so that the pipes form a kind of steps, and four superposed stars fill up the whole section, the pipes of the fifth star lying exactly over those of the first star, and so on. The acid is thus compelled to run all round the pipes and to splash on to the pipes lying below. The pipes have different inclinations, in order to better divide the acid. [Such pipes soon crack, and the whole apparatus then collapses.]

Vol. I. p. 583. *Employment of Lunge-Rohrmann plates in Glover towers.*—An excellent application of these plates has been made in a case where it was necessary to bring about the denitration at the lowest possible temperature, in order to avoid losses by the ammonia present in the gas-sulphur (spent oxide) employed. A small tower of only 13 layers of plates was put on the top of the ordinary Glover tower; the gases leave the latter at  $90^{\circ}$  C., and the plate-tower at  $60^{\circ}$  C. In spite of this slight difference of temperature and of the small height of the plate-tower, it was found to perform 80 per cent. of the denitrating work. Hence the plate-towers must be considered excellently adapted for this class of work, if they can be kept clear of flue-dust (which in the above case was retained by the old Glover tower). They must, however, not be flushed out while hot with cold water, which causes the plates to crack (comp. also *supra*, p. 778).

Vol. I. p. 627. *Theory of the vitriol-chamber process.*—Ostwald (Discussion at the Congress of Electro-chemists, 1895) contends that the part played by the nitrous acid is not that of an oxygen carrier, and that the intermediate products containing it are only accidental. It simply acts as a "catalytic substance" in greatly hastening the otherwise too slow oxidation of sulphurous acid by atmospheric oxygen. [This opinion is contradicted by the fact that the intermediate product, *i. e.* nitroso-sulphuric acid, is present in every vitriol-chamber in enormous quantities, and that even a slight diminution of that quantity leads to a sharp check in the acid-forming process.]

Vol. I. p. 627. *Nitrogen peroxide in chamber-gases.*—Benker (comp. Kienlen, *Monit. scient.* 1895, p. 321) injects  $\text{SO}_2$  into the last chamber, in order to remedy the drawback, occurring in the

"forced work" (Vol. I. p. 373), that vapours of  $N_2O_4$  are formed which, as he believes, are not sufficiently absorbed in the Gay-Lussac tower. These are to be reduced to  $N_2O_3$  by  $SO_2$ . This is evidently the same principle as that involved in Benker and Lasne's former process (Vol. I. p. 557); the only difference is that they injected the  $SO_2$  immediately in front of the Gay-Lussac tower, and that Benker now sends it into the last chamber. In regular work this process can only act injuriously; but in cases where there is an excess of  $N_2O_4$  it may do good.

Vol. I. p. 634. *Influence of the impurities found in commercial Sulphuric Acid.*—According to Deutecom (Chem. Zeit. 1892, p. 574), a minute quantity of *mercury* makes sulphuric acid less suitable for pickling brass objects. *Nitric acid* causes wool to be stained yellow in the "carbonizing" process. *Platinum* renders the acid unsuitable for electrical storage-batteries. *Iron* sometimes causes a pink colour, which is removed by a little nitric acid, sometimes even by the action of atmospheric air. [This looks as if the pink colour was not caused by iron, but by selenium.]

Vol. I. p. 635. *Arsenic found in different parts of the chamber-system.*—Stahl (Zsch. f. angew. Chem. 1893, p. 54), in working Spanish pyrites, found in the acid of the first chamber 0.16 per cent.  $As_2O_3$ , in the second 0.01 per cent., in the third 0.007 per cent., and in the last chamber only a trace. When working purer pyrites from Virginia or New England, the acid of the first chamber contained 0.005 per cent.  $As_2O_3$ , the second nothing, the average 0.002 per cent., all calculated on acid of 66° Bé.

Vol. I. p. 642. *Purification of Sulphuric Acid from arsenic.*—This, according to H. F. Stahl, is most conveniently effected as follows:—The acid is diluted to 76° or 82° Tw., heated to 80° C., and a solution of barium sulphide of 12° Tw. is run in at the bottom of the vessel in such manner that no  $H_2S$  escapes. The  $As_2S_3$  is filtered off on a sand-bed, placed on a layer of quartz lumps, and thus the arsenic is reduced to 0.01 per cent. As. But as the acid, on standing in the filter, again takes up a little arsenic, it is treated with gaseous  $H_2S$ , and is thus reduced to 0.005 per cent. As, which cannot be attained either with  $BaS$  alone or with  $H_2S$ , but only by the successive application of each.

*For electrical storage-batteries* sulphuric acid should be as free from arsenic as possible. Arsonval endeavours to attain this by

pouring 4 or 5 c. c. of colza oil on to a litre of sulphuric acid, which is to form glycerine-sulphuric acid, and to precipitate the arsenic, lead, &c., in the form of soaps [?]. Gothard prescribes the same addition; the mixture is to be shaken up, allowed to stand for 12 hours, poured into water, and, after cooling, the sticky mud must be skimmed off the purified acid (Chem. Zeit. 1892, p. 163).

Vol. I. p. 650. *Purification of Sulphuric and Hydrochloric Acid from arsenic, &c. by sulphuretted hydrogen.*—Whitehead and Gels-tharpe (Engl. pat. 18940, 1894) obtain  $H_2S$  for this purpose by treating liquor from partially oxidized vat-waste with  $HCl$ . The mixture thus evolved, containing  $H_2S$ ,  $SO_2$ , [1], and atmospheric air, is alleged to act better than pure air. [This process is not patentable. The employment of vat-waste for this purpose has been expressly mentioned in this connexion in my Treatise, which appeared in 1891; nor is the partial oxidation patentable, since vat-waste, such as would be available, always has been, and always will be, partially oxidized; nor is it essential whether the waste itself, or the yellow liquor draining from it, is employed. The assertion that  $SO_2$  occurs in these gases at the same time as  $H_2S$  is of course wrong, since it is not the question of mere traces. The apparatus described by the inventors presents no specially remarkable features.]

Vol. I. p. 652. *Purification of Sulphuric Acid from nitrogen acids by ammonium sulphate.*—Lunge and Abenius (Zsch. f. angew. Chem. 1894, p. 609) show that *nitrous acid*, i.e. nitrosyl-sulphuric acid, is very quickly destroyed by boiling with a proportion of ammonium sulphate of 1  $NH_3$  to 1 acid nitrogen; even with sulphuric acid of  $140^\circ$  Tw., this takes place in five minutes. But *nitric acid* is far more stable; it requires half an hour's boiling with its equivalent of ammonium sulphate, in the case of the strongest sulphuric acid, for its destruction, and many hours' boiling with a large excess of ammonium sulphate in the case of acid of  $140^\circ$  Tw. Hence any contamination with nitric acid must be carefully avoided if the sulphuric acid is to be concentrated in platinum, since some  $HNO_3$  will get into the platinum still in spite of all precautions; but nitrous acid is easily removed at every stage by ammonium sulphate.

Vol. I. p. 658. *Concentration of Sulphuric Acid in lead vessels.*—Wolters (Engl. pat. 18831, 1893) carries this process beyond the usual extent, preventing the action of the acid on the lead by

saturating the acid with lead sulphate. An excess of this is put in and is kept in suspension by mechanical stirring. Most of the dissolved lead sulphate crystallizes out on cooling, and can be used over again.

Vol. I. p. 658. *Concentration of Sulphuric Acid in lead pans.*—At the Freiberg smelting-works the circumstances of the case require the whole of the acid produced, 17,000 tons 50° Bé. per annum, to be concentrated to 60° Bé. in special apparatus, and great experience has been gained with different systems. These have been described in detail by Junge (Jahrb. f. Berg- u. Hüttenw. in Sachsen, 1892; partly also in Zsch. f. angew. Ch. 1893, p. 61).

Part of the work is done by *steam-heated* pans, which to some extent differ from those described in the text (Vol. I. p. 676), and which are minutely described in the original. They are flat-bottomed boxes, lined with 5 millim. lead, about 10 ft.  $\times$  4 ft. 3 in. and 14 inches deep, with a coil of lead pipe,  $1\frac{1}{2}$  in. bore,  $\frac{1}{8}$  in. thick, 184 ft. long, resting on loose pieces of lead-piping. Six such pans are combined in a set, communicating by overflows; the acid runs in at one end and out at the other. The steam-pressure is best not exceeding  $2\frac{1}{2}$  atmospheres. The temperature rises in the first pan to 125°, and does not go above 128° in the last. The strength of the acid (entering at 51°·4 Bé.) in the six pans is respectively: 53°·9; 56°·1; 57°·4; 58°·6; 59°·4; 50°·2 Bé. Hence a comparatively low pressure, far below the boiling-point of the acid, suffices for concentration; but this involves slower work and much more plant than concentration by direct firing. The cost of repairs is slight so long as the apparatus is new, but subsequently it is very considerable. The thickness of the steam-coils corresponds to a strain of 60 atmospheres in the cold; in spite of this they later on become bulged out and burst with a pressure of only  $2\frac{1}{2}$  atmospheres. This is caused partly by the action of steam from within and hot acid from without, partly by the gradual diminution of the tensile strength of the lead used at that high temperature. Lead alloyed with  $1\frac{1}{2}$  per cent. antimony (hard lead) cannot be used, as it is quickly destroyed by hot sulphuric acid (comp. the investigations carried out by myself, together with E. Schmid, quoted above, p. 764). This occurs chiefly in the places where the hard lead is in contact with soft (pure) lead and galvanic action sets in, but this is noticed only at higher temperatures, not with apparatus worked at the ordinary degree of heat. The steam-

pans are gradually very much impaired in their efficiency by lead-mud, &c. settling between the coils; they then furnish less and weaker acid. Hence their use cannot be recommended, except where it is absolutely necessary to avoid any injury to vegetation, which is certainly altogether excluded here, as well as any loss of acid. But they are far more costly, both to erect and to work, than directly fired pans.

The Freiberg *bottom-fired pans* are about 6 ft. 6 in. long, 3 ft. 3 in. wide, and 8 in. deep. They are supported by  $\frac{1}{2}$  in. cast-iron plates and are arranged in tiers, the fireplace being underneath the strong bottom pan and the acid running in at the top pan. These pans furnish a uniformly strong acid, and consume only two-thirds as much fuel as the steam-pans. They suffer, however, under the disadvantage that the first, strong, pan is quickly worn out. [It is strange that Junge does not even mention the arrangement, represented as the only rational one in Vol. I. p. 667, in which the fireplace is situated underneath the *weak* pan, in order to lessen the wear and tear.] Sometimes the pan-bottom is suddenly decomposed, the cause of which is unknown. [The explanation of this phenomenon is given by the above-quoted investigations of Lunge and Schmid, published about the same time as Junge's paper, and abstracted above, p. 764.] In normal work the temperature of the acid running off is 200° C. [This is much higher than has been hitherto observed, Vol. I. p. 607, and this may explain the great wear and tear.]

Very good results have been obtained with a system in which the fireplace is arranged underneath a platinum dish, covered with a water-cooled dome, and protected by a brick arch below. From this the fire passes underneath the lead pans, in which the acid thus never exceeds 160° C. or 58° Bé. The sudden destruction of the first pan never happens in this case. After 15 to 20 weeks' use it begins to leak slightly, so that the acid can be drawn off before any trouble arises. The first pan now lasts 3 or 4 months, the second 2 or 3 years, the others 5 years, and they can be replaced within 12 hours at a trifling cost. This apparatus, inclusive of the platinum dish, costs about as much as the steam apparatus, inclusive of the steam-boiler; it requires much less space, is quite as safe, and furnishes a stronger and more uniform acid, with a much smaller consumption of fuel.

Vol. I. p. 666. *Lead pans fired from below.*—MacDougall

(Engl. pat. 21778, 1894) employs perforated cast-iron plates for supporting the bottom, preferably in the shape of a grid with longitudinal and transverse rills, leaving diamond-shaped holes. This indeed, according to 'Alkali Report,' no. 31, p. 54, prevents a local overheating of the pan-bottoms, which readily occurs with solid cast-iron plates, and the pans do not show any buckling even after prolonged use.

Carulla (Journ. Soc. Chem. Ind. 1893, p. 15) interposes between the lead and the ordinary solid 1-in. cast-iron plate a copper plate  $\frac{3}{8}$  in. thick, which, owing to its good conduction of heat, very efficiently prevents local overheating of the lead, without interfering with the transmission of the heat.

Vol. I. p. 689. *Concentration of Sulphuric Acid by glass retorts on the intermittent plan.*—The construction and working of the plant at the Mülheim works have been very minutely described by Lütty (Zsch. f. angew. Chem. 1892, p. 385). This communication would be very important and interesting if the intermittent plan were not now universally recognized as far too expensive, and therefore antiquated; I must therefore refer those still interested in it to the original or to the translation in Journ. Soc. Chem. Ind. 1893, p. 153. The plant described by Lütty (erected by an English chemist) seems to have been even less economical than some others, and is a warning example against the whole system.

Vol. I. p. 692. *Continuously working glass retorts.*—Penniman (Amer. pat. 469439) employs in a set of retorts arranged stepwise a current of air, which keeps the acid continually agitated, and so prevents their breaking.

Vol. I. p. 692. *Cost of concentrating Sulphuric Acid in glass retorts.*—According to a very interesting comparative survey by Tate (Journ. Soc. Chem. Ind. 1894, p. 208), to which we shall have again to refer, the cost of a battery of glass retorts on the old system, for making 10 tons in 24 hours, ranges from £800 to £1000, inclusive of condensing-apparatus. The cost of concentrating from spec. grav. 1.76 to 1.838 varies very much; but the fuel averages 13 to 14 cwt., and the wages 4s. 6d. per ton of strong acid. The breakage varies extremely at different places.

With the Gridley-Chance system the cost of two sets of four retorts each, for making 23 to 25 tons acid per week, is £200, and

£100 for the building. It is easy to make acid of 95 per cent.; 97 per cent. acid requires more time. The cost of labour is only from 2s. to 3s. per ton of strong acid; of coal only two-thirds of the quantity required by the old system is necessary, say 10 to 12 cwt. per ton. [This does not agree with the above statement, and later on only 5 cwt. is spoken of.] The breakage is only about one retort to 180 or 200 tons of acid, or, say, 1s. per ton (a retort costs 25s.; in discussing the paper it was mentioned that the breakage is frequently much higher). Extra-concentrated acid is more easily made in glass than in platinum retorts. Acid contaminated by suspended or dissolved impurities is not easily concentrated by this system, as it causes much breakage.

Vol. I. p. 692. *Retorts* having the lower half composed of glass and the hood of any suitable material are described by Schofield (Engl. pat. 19780, 1891).

Vol. I. p. 694. *Négrier's system of concentrating Sulphuric Acid in porcelain dishes* is minutely described by Kretzschmar in Chem. Zeit. 1892, p. 418. The gases from a set of four furnaces pass underneath three sets of lead pans, where they concentrate the acid up to 134° to 142° Tw., and heat them to 145° or 149° C. Each furnace produces 25 cwt. of acid of 93 per cent. daily, with an expenditure of 23·5 per cent. of rather low-grade English coal. The breakage of dishes per month was at first 5, out of a total of 64, costing 4s. each; but this was greatly lessened when the cast-iron bed-plates were replaced by fire-clay slabs. The acid vapours from each set of two furnaces pass into a lead condenser, then into a cooling-worm, and eventually into an upright pipe, in which the necessary draught is produced by a jet of compressed air. The Négrier apparatus has the advantage of allowing the use of impure and nitrous vitriol, but it requires much more space, labour, and coal than platinum stills.

Vol. I. p. 694. *Concentration in glass and porcelain vessels.*—A system of concentrating sulphuric acid, very similar to Négrier's described in the text (which, as Scheurer-Kestner has pointed out in Bull. Soc. Ind. Mulhouse, 1892, p. 317, was preceded in 1887 by an American patent of W. H. Adams), has been recently described by Webb and also exactly on the same lines by Levinstein. Both of these gentlemen employ batteries of glass beakers arranged in steps, but Webb has recently replaced the lower portion of the battery by porcelain beakers.

Fig. 230.

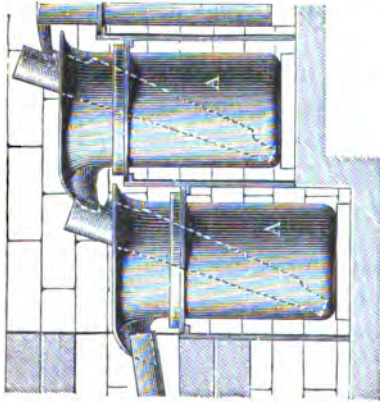
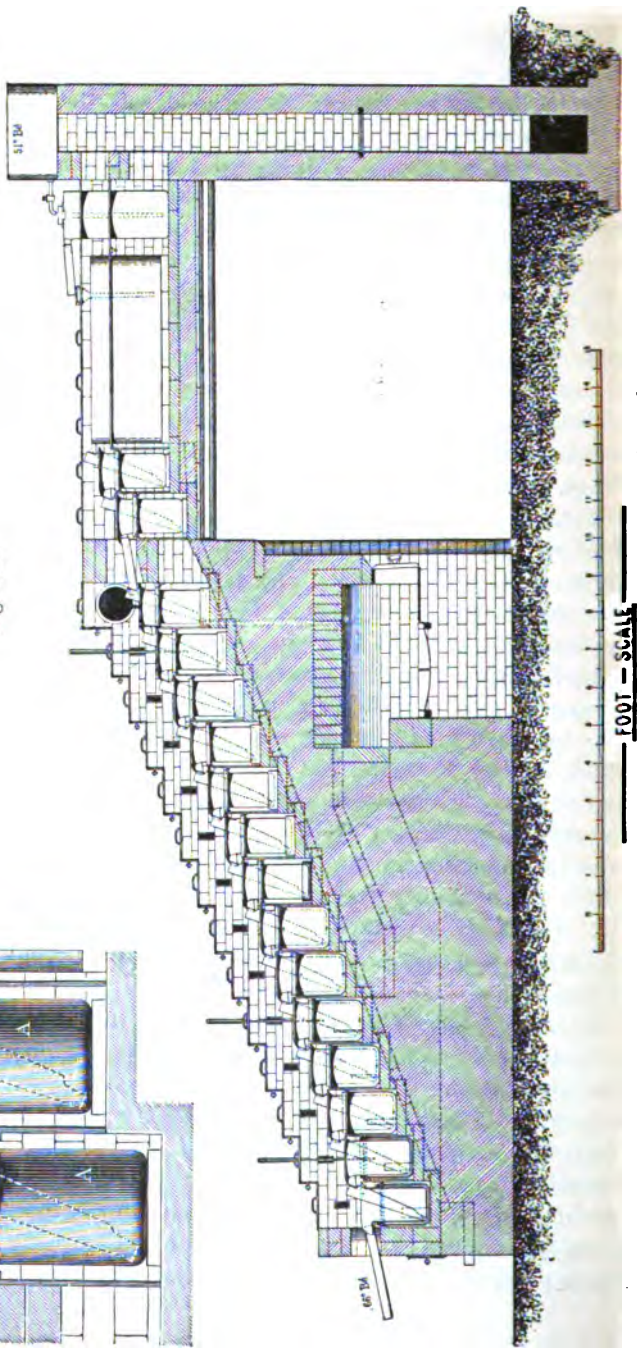


Fig. 235.





Webb's English patents are Nos. 2343, 17407, and 18891, all of 1891. As figs. 235 and 236 show, his apparatus consists of 14 or 16 glass (or porcelain) beakers, A, A, arranged one above the other, about 11 in. wide and 21 in. high, with overflow lips communicating with movable, tapering glass pipes placed in a slanting position in the next lower beaker, so that the acid flows from each beaker on to the bottom of the next, and from the last of these through a cooler into the vessels where it is to be stored.

The patent No. 2343, 1891, runs as follows:—A series of glass vessels are placed on slabs, arranged in steps, in a heating-chamber; the vessels are enclosed near their upper edges in iron plates or slabs, corresponding to the bottom. In each of these vessels is placed at an angle a loose tapered glass tube, reaching from the spout of one vessel to the bottom of the next lower vessel, where it is provided on its side with an outlet slit. The fire-gases pass first into combustion-chambers on one side of the heating-chamber, and from thence into the space left round the glass vessels. The weak liquor is fed into the tube of the uppermost vessel and displaces a certain amount of acid, which will overflow into the tube of the next vessel, &c., thus causing a thorough interchange in the liquor to be evaporated. The concentrated acid is delivered from the last vessel of the series.

Much stress is laid on the fact that the acid always flows on to the bottom of the next lower beaker, where it forces the already concentrated acid upwards and is well mixed with it.

The cost of an apparatus of 14 glasses, apart from patent royalty, is from £60 to £100. Usually two sets are built together. 14 glasses produce per hour a carboy of acid of spec. grav. 1.838 from acid of 1.74, with consumption of less than  $\frac{1}{2}$  cwt. of coke. One man can attend to 4 sets of 14 glasses each, in which case the cost of labour is only 2d. per carboy. Each set makes 5 or 6 tons of strong acid per week from acid of 1.60, or 11 to 12 tons from acid of 1.74.

At first the breakage was very considerable, so long as all beakers were made of glass, but since the three bottom beakers of each set have been replaced by porcelain vessels the breakage has been greatly reduced. More recently *all* the beakers have been made of porcelain, and since then the breakage is *nil*. The feed of acid is regulated by means of a thermometer placed in the fourth beaker from the bottom. No lead pans are needed for

preliminary concentration. Even the most impure acid, also waste acid from dynamite-works &c., can be worked up. The acid running off in cases of breakage is easily caught and used over again.

Levinstein's patents are: No. 19213, 1892; Nos. 2476 and 2835, 1893; No. 22844, 1894; his apparatus is very similar to Webb's, but the beakers have rounded bottoms and are placed in metal dishes, and the overflow-pipes are modified. According to one of his latest patents, the dilute vapours from the upper portion and the strong vapours from the lower portion of the battery are carried away separately, which appears to be a very rational process.

Quite similar to the above is Bradbury's apparatus, Engl. pat. 22327, 1893, and that of J. W. Scott, Engl. pat. 14215, 1894.

Vol. I. p. 708. *Advantage of the concentric partitions in platinum stills.*—Scheurer-Kestner (Bull. Soc. Ind. Mulhouse, 1892, p. 321) gives data as to the difference produced by working with a Desmoutis still, first without and then with concentric partitions, the acid being forced by the latter to remain longer in the stills in the proportion of 48:62. The data refer to both styles of work:—

	Without partitions.	With partitions.
Make in 24 hours .....	5136	6632 kil.
Concentration of acid .....	92·5	92·5 per cent.
Average strength of distillate ...	36°	11° Baumé.
Weight of ditto .....	2160	2160 kil.
Weight of the corresp. $H_2SO_4$ ...	816	216 „
Percentage of acid distilled .....	15·8	3·2
Weight of coal used .....	1100	1100 kil.
Ditto per cent. conc. acid .....	21·4	16·5
Water evaporated .....	1344	1944 kil.

These undoubted advantages of the concentric partitions are, however, counterbalanced by a greater loss of platinum and more frequent repairs, so that many manufacturers have abandoned this system after having tried it.

Vol. I. p. 721. *Lead hoods for Faure and Kessler's platinum dishes.*—The Chemische Fabrik Rhenania (Germ. pat. 64572) makes these hoods of a long coil of lead tubing, burning the walls together so as to form a tight bell, within the walls of which the cooling-water circulates. This system answers very well, and has

been introduced at a number of factories. It is probably the best now in existence for this special purpose.

Vol. I. p. 722. *Special shapes of platinum stills.*—Siebert (Engl. pat. 9514, 1893) builds platinum retorts with stepped bottoms, on which the acid runs down in cascades. [The rate of concentration and the consumption of coal are very favourable in this apparatus; but it has been abandoned, as the bottom could not be prevented from running dry, and thus the wear and tear became too great.]

Hannetelle (Engl. pat. 22704, 1891) describes four cylinders mounted stepwise, inclined alternately to opposite sides, the acid running downwards through all of them. The "Chapuis still" is constructed on the same principle.

Lasne uses a flat, oblong still, 6 ft. 6 in. long, in which the acid runs from one end to the other in a layer of about 2 inches.

Krell (Engl. pat. 18727, 1894) employs a cast-iron pipe, or a wrought-iron tube, lined with platinum or gold, entirely immersed in a bath of molten lead, through which the sulphuric acid passes in a slow stream. He claims that, owing to the even heating, the decomposition of the acid into water and anhydride is largely avoided, the temperature of the vapours never exceeding the boiling-point to any considerable extent.

Howard, in Boston, Mass., has constructed an automatic regulator for platinum boilers. By means of a float the specific gravity of the acid automatically regulates the feed, and thus acid of uniform strength is obtained. This apparatus was patented in America in November 1893.

Vol. I. p. 725. *Loss of platinum and platinum-gold stills.*—Davies (Journ. Soc. Chem. Ind. 1894, p. 210) states the average loss of platinum = 3s. per ton of strong acid. Sometimes it goes down to 0.34 gram per ton. Formerly it was less than it is now [?]. When making 97 per cent. acid the loss occasionally rises to 20 grams platinum per ton. [Such strong acid should be made in glass or iron retorts, or in boilers made of the Heraeus platinum-gold composition. This composition (comp. Vol. I. p. 728) is now very largely used, especially in Germany and America, and may be regarded as the best kind for apparatus where *pure* acid is concerned, both for entire stills and for pans covered with leaden hoods. The gold coating in the former case must be extended to the whole interior of the boiler, not merely

to the bottom, as otherwise galvanic action sets in at the place where the acid touches both platinum and gold. The Heraeus composition is not adapted for impure acid which forms crusts, as these necessarily cause damage to the gold, and as soon as any platinum is exposed the galvanic action sets in. Otherwise it is excellent.]

*Mercury* is sometimes contained in blende &c., and gets into sulphuric acid (Vol. I. p. 299). If it reaches the platinum stills it may do great harm, as it may there be reduced to the metallic state.

*Prices of platinum stills.*—Hasenclever (Chem. Ind. 1892, p. 30) gives the following table of prices (in marks) of platinum stills per kilogram (the mark=nearly 1s.):—

Year.	Marks.	Year.	Marks.	Year.	Marks.
1869 .....	600	1877 .....	798	1885 .....	1040
1870 .....	600	1878 .....	825	1886 .....	1040
1871 .....	600	1879 .....	900	1887 .....	1040
1872 .....	600	1880 .....	880	1888 .....	1080
1873 .....	837	1881 .....	880	1889 .....	1107
1874 .....	837	1882 .....	890	1890 .....	1970
1875 .....	800	1883 .....	947	1891 .....	1650
1876 .....	800	1884 .....	1013	1892 .....	1250

Vol. I. p. 729. *Crusts in platinum stills.*—The following is the composition of such crusts as observed at a French works, according to private information:—

	Hard, stony crust.	Softer crust, impreg- nated with acid.
Fe <sub>2</sub> O <sub>3</sub> .....	33·60	23·00
SO <sub>3</sub> .....	63·20	63·60
SiO <sub>2</sub> .....	—	0·20
CaO .....	trace	1·10
MgO + Na <sub>2</sub> O .....	trace	0·85
As <sub>2</sub> O <sub>5</sub> .....	trace	trace
PbSO <sub>4</sub> .....	trace	trace
Se .....	trace	trace
Al <sub>2</sub> O <sub>3</sub> .....	trace	—

Vol. I. p. 729. *Concentration of Sulphuric Acid in gilt-copper vessels.*—Gilt-copper stills are proposed by Neuerburg (Germ. pat.

58511), but they are evidently quite impracticable, since all such coatings are more or less porous; at the least break in the gold coating the acid would at once destroy the copper vessel. The Heraeus composition, mentioned in the text and above p. 795, is not simply gilt-platinum (which does not answer), but is a solid gold sheet fused on to a platinum sheet, and this has indeed proved a complete success, and is now introduced at most German and many other works.

Vol. I. p. 730. *Concentration of Sulphuric Acid in iron vessels.*

1st. *Enamelled cast iron.*—Tate (*loc. cit.* p. 790) mentions an apparatus constructed by West in 1883 on the continuous system, with an enamel or porcelain lining; nothing is known as to its success.

Dyson (Engl. pat. 17699, 1893) has made a cascade-apparatus, consisting of iron pans lined with a special enamel, connected by U-shaped siphons, which carry the acid from the bottom of each vessel into the upper part of the next. A set of 18 pans produces 21 tons of strong acid per week. This apparatus is to cost £250, and to require 6 cwt. of coke per ton of acid. Some more details are given in Chem. Trade Journ. xvii. p. 339. Chamber acid of 100° Tw. is employed, and 100 tons acid of 168° Tw. is produced in one apparatus in 43 days, with a consumption of 23½ tons of gas-coke; the wages are £19 9s. 7d., or 3s. 10½d. per ton, which would be greatly reduced if the same men could look after two plants. [Main features in this system are the time which the enamelled iron vessels will last and the cost of renewals.]

2nd. *Wrought iron.*—Tate (*loc. cit.*) gives particulars of an old tar-still, made of ⅜-in. plate, 6 ft. wide and 4 ft. high, in which for several years past a mixture of sulphuric and nitric acid had been concentrated from spec. grav. 1.75 to 1.838, with recovery of the nitric acid. [Perhaps the use to which this vessel had previously been applied had deposited a protective, carbonaceous coating.]

3rd. *Cast iron.*—Tate mentions pots, 9 feet wide and 6 feet deep, 2 in. thick, with cast-iron lids, weighing 11 or 12 tons, in which acid of spec. grav. 1.74 is concentrated within 28 or 30 hours to 96 per cent.; one such pot produces 12 tons of acid. It is allowed to settle and cool for 12 hours, so that one of these pots can be finished every two days. Coal used 2 cwt. per ton, wages 1s. per ton, wear and tear 3s. or 4s. per ton of finished acid.

From time to time the mud consisting of iron salts must be cleaned out, and this represents 4 or 5 per cent. of acid lost. Such a pot costs £60, the lid (which lasts for 3 or 4 pots) £10; the setting £30. Each pot produces from 500 to 600 tons of acid, and is then worth £10 or £15 as old metal. The plant requires very little space and no expensive building. The dirtiest acid can be worked up which can hardly be worked by any other system, and the highest strength can be attained [but the acid will be very impure].

In my report on a visit to America (*Zsch. f. angew. Chem.* 1894, p. 135) I have described the following plants:—In one place they concentrate the acid to 66° Bé. = 93·5 per cent. in platinum, above that, up to 98 per cent., in round cast-iron pans, 3 ft. wide and 2 in. thick, with double flange for a hydraulic joint, in which a water-cooled leaden hood dips. The hydraulic flanges are lined inside with lead, as they are filled with weak acid. Such a pan lasts two months. The acid evidently does not take up much iron, as it is partly used for the manufacture of nitro-glycerine.

At another place they employ a set of three pans: one is made of cast-iron, 4 ft. × 3 ft. area, and two of platinum, all three with lead hoods on the Faure-Kessler principle. In the platinum pans the acid rises to 65½° Bé., in the iron pan to 66° Bé. This acid is only used for purifying petroleum. All three pans are heated by heavy petroleum (spec. grav. 0·833, the residue from the manufacture of paraffin), injected by a steam-jet. The regularity and facility of this kind of heating compensate the excess of cost of coal. The flame, after heating the three pans, passes above the weaker acid contained in two lead pans, each 30 feet long and provided with an inner dry wall and a water-jacket as protection against being burned through. The first lead pan receives chamber-acid of 53° Bé.; the second lead pan brings it up to 61° Bé., the second platinum pan to 65°·5, the iron pan to 66° Bé. Each set furnishes daily 500 carboys or about 20 tons, with a consumption of 900 American gallons, or a little over 3 tons, of heavy petroleum, costing 2 cents per gallon, or 7·5 tons per 100 tons acid. The iron pans last three months.

At another place they have two platinum pans with lead hoods, the upper (weak) pan receiving the direct fire, combined with two specially fired iron retorts, constructed as described in Vol. I. p. 733, viz., a bottom part, 8 ft. × 2 ft. section and 8 inches deep, connected by a flange and rust-joint with a similar shaped, but

only 4 in. deep lid. The fire plays all round, first underneath the pan and then above it, in a 12-in. wide flue. The 6-in. vapour-pipe passes through this. The acid attains to 98 per cent., and is drawn off by means of an iron tap.

In a fourth factory, at Pinole, Cal., there is the following apparatus, for the drawings and description of which I am indebted to the superintendent, Mr. Quinan. Fig. 237 shows the iron pan without cover, seen from above; fig. 238 is a sectional plan through A B, showing the steam-pipe and the outlet-pipe with mud-box; fig. 239 part of the longitudinal section through C D, showing the acid-inlet and the thickened bottom below it; fig. 240 a cross-section at right angles through the inlet. The pan is divided into three compartments by longitudinal partitions which leave openings at alternate ends of the pan, and thus compel the acid to travel in a zigzag manner. Corresponding to these channels, the pan-bottom is bulged outwards, in order to enlarge the heating-surface. The flat cover rests on a rebate formed on the upper edge of the pan, and is luted in this with a mixture of barytes and silicate of soda; it is held in its place by six castings, *a a*, wedged against corresponding lugs, *b b*, on the pan; these lugs also serve as bearers for the pan. The cast-iron vapour-pipe, *c*, 2½-inch bore, is connected by flanges and screw-clamps with a neck formed in the cover; the joint is made by an asbestos washer and the silicate-of-soda mixture. During work the pan lid is tightly covered with asbestos waste, to protect it against cooling and the consequent action of the acid. The acid-inlet is not arranged in the cover, but in a cup, *e*, cast on to the pan; below this the pan-bottom is thickened, as this part is always strongly acted upon. The pans are 5 ft. 6 in. × 1 ft. 6 in. surface and 10 in. deep; the channels are 5 in. wide each, thickness of metal  $\frac{5}{8}$  in.

The acid-outlet is at the cast-iron neck, *f*, opposite which is a cleaning-hole in the pan-lid, with the cover, *d*, luted by silicate-of-soda cement. Neck *f* is joined to the cast-iron pipe, *g*, leading to the mud-box, *h*; from this a cast-iron pipe, *i*, again rises upwards, and is connected by a side-branch with the short platinum tube, *k*, which conveys the acid into a Johnson and Matthey's platinum-cooler. By this arrangement the acid is obtained perfectly clear and free from mud.

This iron pan is connected with two Delplace platinum stills,

18 in. wide and 5 ft. long. The acid enters 62° Bé. strong from the lead pans into the first platinum still. The fire, on leaving the platinum stills, travels underneath seven lead pans; there are also lead pans on the eight sulphur burners. This set of one cast-iron pan and two platinum stills, together with an auxiliary iron pan and platinum still, supplies a set of chambers of 200,000 cubic feet.

The firing of both iron and platinum stills is performed by crude petroleum, sprayed by superheated steam. The introduction of this system, in lieu of a coal-fire, not merely saves labour, but it also increases the turn-out from 9 tons to 13½ tons of 96 per cent.

The duration of an iron pan is from four to eight months. They are rarely used up, but they crack in the places where thick crusts are formed, sometimes without apparent cause, probably in consequence of faults in casting. [Recently chilled cast-iron seems to have given great satisfaction.] Small holes sometimes forming at the inlet can be stopped up by silicate-of-soda cement.

The vapour-pipe, *c*, leads to a condenser constructed of platinum and lead. Formerly it had to be protected against cooling and quick corrosion by a thick asbestos coating; but later on a cast-iron mixture was invented which lasts almost indefinitely even without such protection [probably chilled cast-iron].

During work a deposit is formed at the bottom, principally consisting of ferric sulphate, which is removed once a fortnight. The pan is emptied, the cover removed, the outlet *f* is closed, the pan is filled with water and heated to boiling. The crusts, which are sometimes ½ in. thick, are then chiselled off. Such crusts of course greatly diminish the heating efficiency. In the first channel, where the fresh acid enters, there is not much deposit—on the contrary, the iron is slightly acted upon; and the ferrous sulphate, together with that issuing from the chambers in large quantities (comp. below), is deposited in the second and third channels. A little mud is always carried along by the acid, but is deposited in box *h*.

The acid made by this apparatus, remarkable to say, contains less iron than that formerly concentrated to 96 per cent. in platinum stills at the same works. No doubt this is caused by the fact that they now bring up the acid to 97 or 98 per cent. But it is possible to turn out 95 per cent. or even 94 per cent. acid in this apparatus.



Fig. 237.

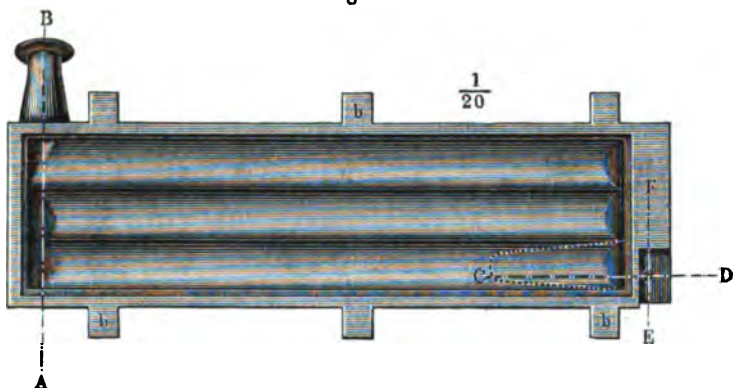


Fig. 238.

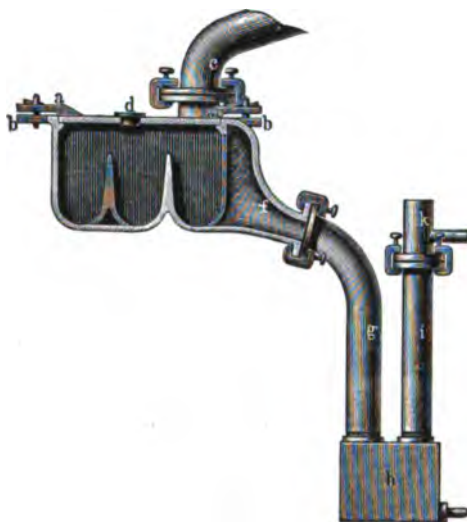


Fig. 239.

Fig. 240.

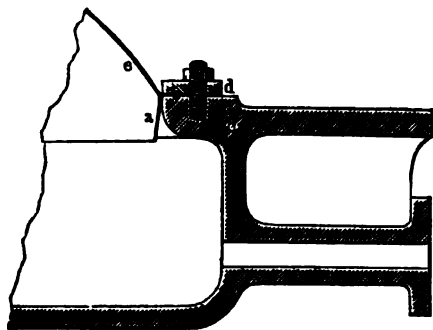




platinum rim, protects the cast-iron from the drops of weak acid falling from the top. A cast-iron pan supplying 5 tons of acid in 24 hours weighs 5 cwt.: it yields on the average 12·7 grams iron to 100 kilograms acid concentrated from 92·5 to 96 per cent. The platinum pan, in which the previous concentration to 92·5 per cent. is effected, suffers very little indeed. The concentration in iron is not suitable below 95 per cent. or much above this point.

For this reason Scheurer-Kestner prefers the following *combination of a cast-iron pan with platinum dome* (Germ. pat. 61331; Bull. Soc. Ind. Mulhouse, 1892, p. 320). Fig. 242 shows again the arrangement of protecting the iron from drops of weak acid by the platinum apron *a*, and of pruning the joint by means of the platinum flange *b*, held between the iron flanges *c* and *d*. But here the platinum continues into a real hood *e*, closed at top in the

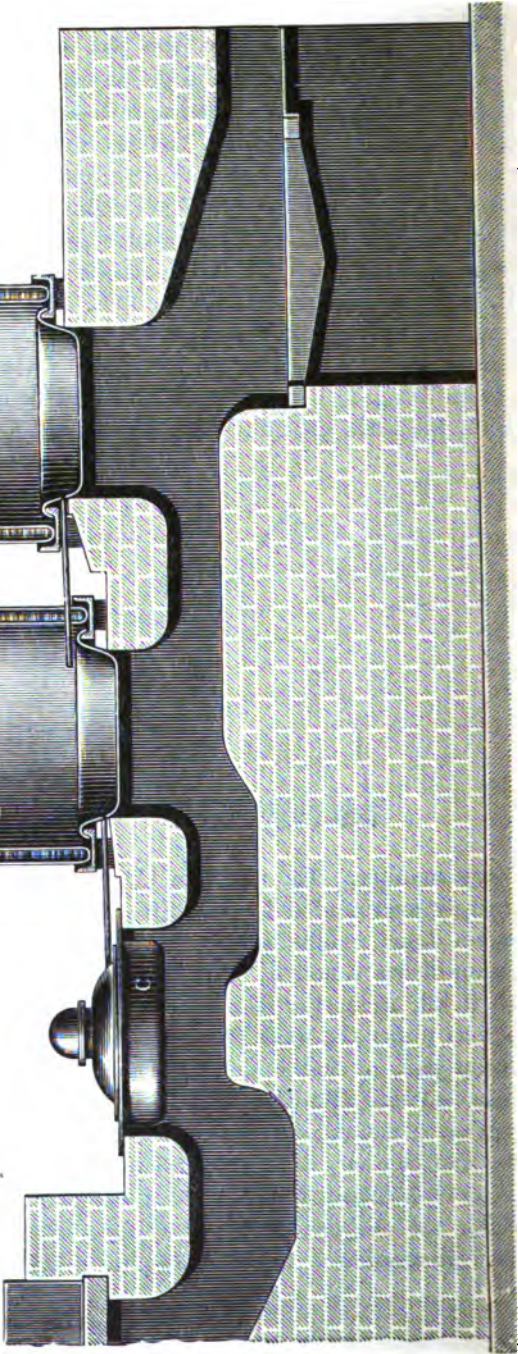
Fig. 242.



ordinary manner. The iron pan C, which weighs 250 kil., must be entirely surrounded by the fire, as shown in fig. 243. The platinum dome weighs from 8 to 8·5 kil., and the preceding two platinum dishes B and A, provided with Faure and Kessler hoods, weigh 9 kil. each, the connection-tubes about 2 kil. The fire plays first under the weak platinum pan, then under the stronger platinum pan, at last under the iron pan. Such an apparatus furnishes 4½ tons of 95 per cent. acid in 24 hours, with less than 0·15 gram platinum lost for each ton of acid; and the concentration can be easily driven to 97·5 per cent.

In the 28th Alkali Report, p. 55, Graham's process is mentioned, in which the concentration takes place in a series of cast-iron dishes. It was found that hot sulphuric acid, in thin layers, in

Fig. 243.



contact with cast-iron, tends to dissociate into  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , so that from a certain point the acid becomes all the weaker the longer and more strongly it has been heated. The dissociation is evidently caused by the superheating of the iron, which becomes much hotter than the platinum. This observation proves the advantage formerly pointed out and again observed in fig. 243, of causing the flame to travel in the same direction as the acid, so that the strongest acid is not in contact with the hottest part of the flame.

Krell (Fr. pat. 241806) passes the vapours formed in the concentration or distillation of sulphuric acid through a tubular cooler placed in a bath, which produces a preliminary heating of the acid, and only subsequently through the final cooler. Thus the latter is less acted upon and there is less dissociation of vapour.

Vol. I. p. 737. *Concentration of Sulphuric Acid by hot gases.*—Fonteuille (Germ. pat. 37713) causes hot air to issue by means of many holes from a pipe at the bottom of a vessel filled with sulphuric acid; the vapours pass in a zigzag manner over several plates, over which fresh acid is running down. [It is not stated what material the vessel is to consist of. This proposal is not sufficiently worked out to be practical, and the utilization of the hot air will hardly be very efficient.]

A process which has been thoroughly worked out, and is now introduced at a number of French and German factories, is that of L. Kessler (Engl. pat. 19215, 1891). I am indebted for the following particulars, as well as the drawings figs. 244 to 246, to the inventor, and I have myself seen the process in operation at Clermont-Ferrand.

The task in question requires several conditions to be fulfilled. The current of hot air must be brought into contact with a sufficiently large surface of liquid to immediately reduce its temperature to a great extent. The air must then be completely saturated with steam and acid vapour. The apparatus must not merely resist the action of the hot air and hot acid, but it must be constructed in such manner that the inevitably formed deposits and crusts do not give any trouble. Under these circumstances the acid can be concentrated far below its boiling-point. In order to produce acid of 95 per cent., boiling at  $284^\circ \text{C.}$ , the temperature need not exceed  $170^\circ$  or  $180^\circ$ ; for the most highly concentrated acid, boiling at  $320^\circ$ ,  $200^\circ$  to  $230^\circ$  is sufficient.

In order to express both functions of this part of the apparatus visible at *c*, Kessler calls it "saturex," because it saturates the fire-gases with acid vapours, and it extinguishes the greatest part of their heat. The gases enter the "saturex" at 300° to 450° C., and leave it at 150°. The acid vapour contained therein is kept back in the "recuperator" mounted above the "saturex." This part of the apparatus entirely resembles the dephlegmating column employed in the rectification of spirit of wine. It is fed with chamber-acid, previously employed for cooling the hot, strong acid issuing from the "saturex." This acid is divided over the numerous holes of the top plate, and gradually descends on to the four lower plates of the recuperator. In doing so it meets the hot air and vapour issuing from the saturer, and drawn through the liquid acid by applying suction at the end. In the recuperator the temperature sinks to 85° C.: this causes nearly the whole of the acid vapour to condense, while the steam is not condensed, nor is there much fresh formed here. This is important, since any concentration of the acid in this place would cause deposits which would soon obstruct the holes in the plates.

Although the gases escaping from the recuperator contain next to no real acid vapour, they contain some acid in the shape of *mist*, as well as some vapour of sulphuric anhydride. This mist is retained by two boxes filled with dry coke; a little water condensing here converts the  $\text{SO}_2$  into  $\text{SO}_4\text{H}_2$ . The weak acid thus formed may be passed through the recuperator. The gases now issue into the air, moderately warm and perfectly free from acid, but charged with all the steam driven out of the chamber-acid. The distilling acid is thus completely condensed without the necessity of employing any cooling-water.

Figs. 244 and 245 show the apparatus. Fig. 244 is a longitudinal section through line J K; fig. 245 a cross section through the "saturex" according to line *m, n*; fig. 246 an enlarged section through some of the plates of the "recuperator." *a* is the fire-place, here shown as a sample grating, but in reality a gas-producer, with gas-coke as fuel. The fire-gases pass through a cast-iron pipe *b*, flattened below so as to cover the whole breadth of the saturer *c*. This is a trough, composed of acid-proof stone slabs, surrounded by a thick lead jacket and placed upon an open foundation. The stone must resist hot acid and hot gases, *e. g.* volvic lava; but even if it were somewhat porous, the lead jacket would retain any acid penetrating through the stone, a little sand

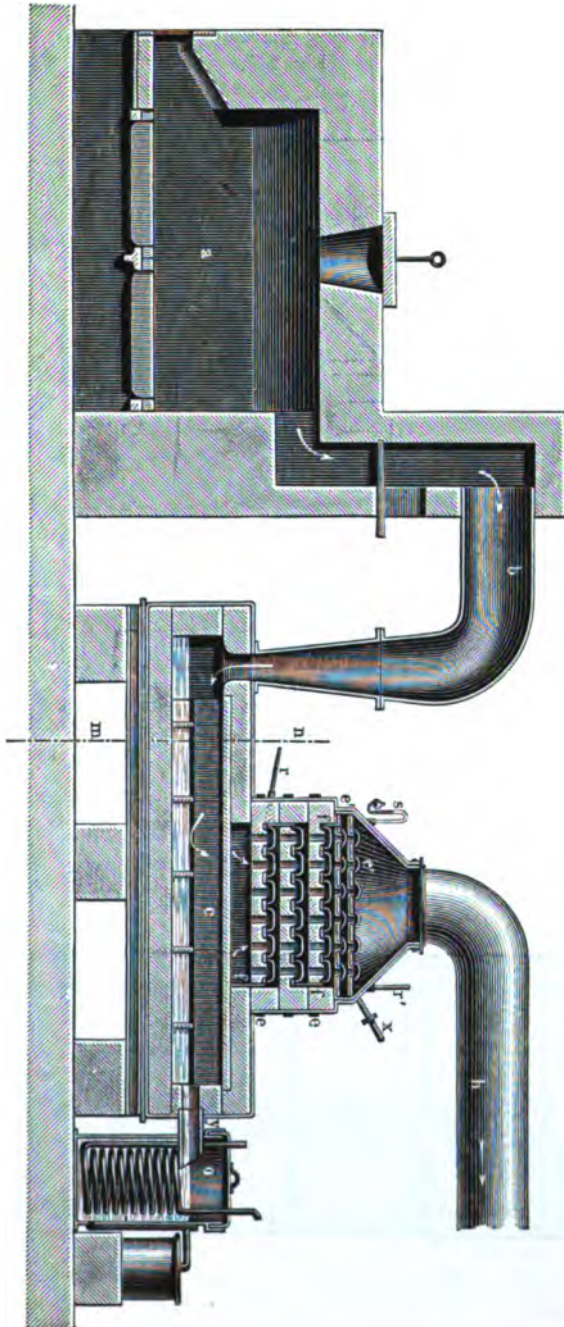


Fig. 244.



Fig. 245.

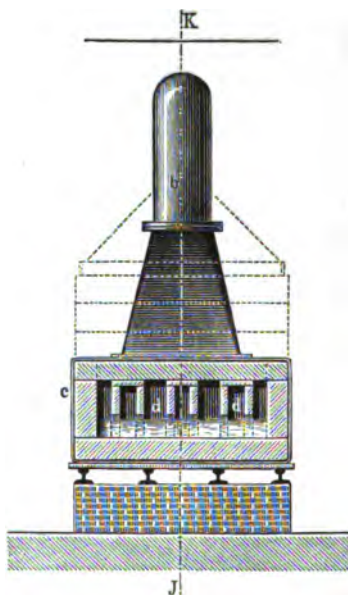


Fig. 246.





being put between the stone and lead. The latter in actual work feels only moderately hot. Between the bottom and the cover of the "saturex" there are several thin partitions, *d, d*, which force the fire-gases, entering at  $300^{\circ}$  or  $450^{\circ}$  C., to circulate over the level of the acid in *c*; when passing from one of these flues to another they are forced almost through the acid itself, and are therefore quickly brought down to  $150^{\circ}$  C.; the acid just as quickly gives up its water and even some acid vapour, and continuously runs off at *y* in the concentrated state into a cooler *o*.

The "recuperator" contains three lower stone plates, *e, e, e*, and two upper lead plates, *e', e'*, all of them arranged as shown in fig. 246. Each plate has 100 holes with somewhat raised margin, so that a thin layer of acid remains standing upon it. The caps *g, g*, made of porcelain with jagged edges, produce a hydraulic seal or at least a great resistance to the passage of the air. The acid arrives as chamber-acid of spec. grav. 1.58 through pipe *x*, and by the overflows *f, f* it runs from one plate to another, finally into the saturex. The gases coming from the latter are by an injector drawn through the holes, from underneath the porcelain cups *g, g*, and are thus brought into intimate contact with the liquid. *r, r'* are thermometers, which serve for regulating the work: the lower, *r*, ought to show about  $150^{\circ}$  C.; the upper, *r'*, about  $85^{\circ}$  C. *s* is a pressure-gauge for the aspiration; *h* the pipe leading to the coke-boxes. The concentration can be driven to 98 per cent.  $\text{H}_2\text{SO}_4$ , and the most impure Glover acid can be used, because in the recuperator there is no evaporation, and therefore no formation of crusts; and in the saturex the latter can collect for a long time without interfering with the process, and can be removed through cleaning-holes with hardly any interruption of the work. The fuel consumed is 8 parts small gas-coke for the gas-producer and 3 or 4 parts coal for raising steam for the exhauster, to produce 100 parts acid of 1.838 from such of 1.58. There is no weak acid, no cooling-water; the apparatus takes up very little space and requires hardly any repairs. The acid is quite limpid and free from nitrogen compounds.

Falding (Engl. pat. 17602, 1893) constructs the pyrites-kilns with hollow walls, by which the air passing through is heated, and can at will be introduced below the grates. The hot burner gases are used for concentrating sulphuric acid, by passing them first into a small tower, consisting of specially acid- and heat-proof

material, surrounded by a somewhat distant lead shell. This tower is placed between the burners and the Glover tower, and receives the acid coming from the latter, which is here concentrated to 66° Bé. The gases pass first into this intermediate tower, then into the Glover tower. [This process is very cheap, but the acid cannot be obtained in a state of great purity.]

Vol. I. p. 738. *Concentration of Sulphuric Acid in a vacuum.*—The drawbacks hitherto noticed in this process are to be avoided as follows, according to J. Meyer (Germ. pat. 71580.) He combines a lead vessel with an iron vessel; the latter, which receives the acid in an already concentrated state, communicates with the air-pump. The pan-bottom is slightly inclined to one side. The dilute acid comes in contact only with lead, the strong acid with iron or platinum. The concentrating-apparatus is best connected with a distilling-apparatus working at the same vacuum, and continually receiving the concentrated acid through a siphon. [It is not shown here how the old difficulty of making the lead stand the outer atmospheric pressure is to be overcome.]

Brown and Georgeot (French pat. 241815) state a theory as to the concentration *in vacuo* in which there is nothing new.

*Concentration of Sulphuric Acid by Electricity.*—Bucherer (Chem. Zeit. 1893, p. 1597) makes the following calculation:—The production of 100 kil. acid of 66° Bé. from 117 kil. acid of 60° B. requires 32,679 large calories, corresponding to

$$\frac{32679 \times 4.2 \times 10^3}{736 \times 3600} = 44.2 \text{ electrical H.P. hours;}$$

calculating the electrical H.P. hour =  $\frac{1}{4}$ d., the above is equal to £1 per ton (on the large scale). Further estimates of the amperage and voltage, the platinum surface, &c., must be passed over here as being entirely hypothetical.

Häussermann and Niethammer (Chem. Zeit. 1893, p. 1907) have made actual experiments on this point. As might be expected, only alternating currents can be employed, since otherwise an electrolysis takes place. The concentration is very easy, but requires 1490 watt-hours per kil. This seems to exclude every possibility of practical application.

Peuchen and Clarke (Engl. pat. 24739, 1893) propose both purifying and concentrating sulphuric (and acetic) acid by the electric current, ultimately proceeding up to distillation. They

proposed electrodes mechanically revolving round a hollow shaft within the boiling acid! A fresh patent of theirs (Germ. pat. No. 83526) describes stationary electrodes for the same purpose.

Wacker (Engl. pat. 3183, 1895) proposes concentrating sulphuric acid by electricity, with introduction of  $\text{SO}_2$ .

Vol. I. p. 772. *Cost-price of Sulphuric Acid in America.*—Stahl (Zsch. f. angew. Chem. 1893, p. 54) considers former statements of Adams and Kelley to be erroneous. According to him, the cost of producing chamber-acid of  $50^\circ$  Bé. in the east of the United States is as follows (in bulk) :—

*A. From Brimstone.*

2.5 tons brimstone (5600 lbs.) at \$21 .....	\$52.50
225 lbs. nitrate of soda .....	4.50
200 lbs. sulphuric acid $60^\circ$ Bé. at \$0.40 .....	0.88
4 men, including firemen .....	6.00
Wear and tear of burners, chambers, buildings...	5.40
Repairs.....	2.70
Coals, lighting, &c. ....	2.00
Management .....	5.00
Capital interest .....	5.00
<hr/>	
13.5 tons chamber-acid cost .....	\$83.98
1 ton           "           " .....	6.22

*B. From Pyrites.*

5.5 tons pyrites (37 per cent. avail. sulphur) at \$6 .....	\$33.00
180 lbs. nitrate of soda .....	3.60
250 lbs. sulphuric acid $60^\circ$ Bé. ....	1.00
Breaking pyrites and removing cinders .....	1.40
6 men, including firemen .....	9.00
Wear and tear of burners, buildings, chambers	5.50
Repairs.....	2.75
Coals, lighting, &c. ....	2.00
Management .....	5.00
Capital interest .....	5.50
<hr/>	
11 tons chamber-acid cost .....	\$68.75
1 ton           "           " .....	6.25

The purification from arsenic, if there is very little present, costs 10 cents per ton.

Hence the costs are about the same, if a ton of pyrites with 37 per cent. available sulphur costs \$6.00, that is \$16.20 for the sulphur contained therein, against \$21 for Sicilian sulphur. The difference of \$4.80 represents the lower value of available pyrites sulphur in comparison with Sicilian brimstone. In the case of Spanish or other pyrites rich in arsenic, the difference in value must be taken = \$1.50 more, or = \$6.30. If, for instance, such pyrites with 47 per cent. sulphur costs \$8, the sulphur therein costs \$17.00 per ton, and this is the equivalent of a price of \$23.30 for Sicilian sulphur.

*Cost of manufacturing Sulphuric Acid from Pyrites and Sulphur in the United States.*—From comparative tables which William Wilke, M.E., and Dr. H. P. Weidig, of Newark, have drawn up, I quote, with their permission, the following figures, choosing a medium plant for producing 10,000 tons of sulphuric acid per annum (evidently chamber-acid of about 50° Bé. is meant) :—

	PYRITES.	SULPHUR.
1 Glover tower .....	12×12×25 ft.	1: 12×12×25 ft.
2 Gay-Lussacs .....	6×35 ft.	2: 6×35 ft.
32 Furnaces.....	5 ft. kilns.	1: 16×20 ft. Furnace.
Cost of whole plant (frame build- ings) .....	58,000 \$	50,000 \$
Cost of whole plant (brick build- ings) .....	73,000 \$	62,000 \$
Pyrites 49 % avail. S @ 7 \$ (long ton) .....	3776.68 tons. 26436 \$	
Sulphur @ 17 \$ per 2000 lbs. ...		2075 tons 35,275 \$
Nitre @ 2 c. per lb. ....	1660 "	1660 "
Coal for air and steam .....	2400 "	1800 "
Total cost of material .....	30,496 "	38,735 "
Labour: 1 manager .....	1500 "	1500 "
" chambermen .....	(2) 1400 "	(2) 1400 "
" furnacemen.....	(4) 2200 "	(2) 1100 "
" labourers.....	(4) 1600 "	(1) 400 "
Total cost of labour .....	6700 "	4400 "
Repairs .....	1000 "	700 "
Interest 6 % on plant and work- ing expenses .....	6180 "	6000 "
Insurance, taxes, water, and office expenses .....	6342 "	6200 "
Depreciation of plant.....	(2½%) 1300 "	(1½%) 1120 "
Total cost of yearly output .....	50,718 "	56,035 "
" per ton acid .....	5.07 "	5.60 "

Vol. I. pp. 774 and 809. *Utilization of pyrites-cinders and purple-ore in blast-furnaces.*—Henzel (Germ. pat. appl. H, No. 12573) mixes pyrites-cinders with from 5 to 40 per cent. ground clay and a little water, and charges the mixture by means of spades, or previously moulded into bricks, into a blast-furnace. The powdered ore is kept together by a superficial fusion of the aluminium silicate, but remains porous and permeable for the reducing gases.

[One cannot understand how such a simple application of extremely old technical principles could form the subject of a patent.]

The Georgs-Marien-Hüttenverein (Germ. pat. 61061) heats bricks, moulded from pyrites-cinders, by a special fire to the sintering point.

Wüst (Germ. pat. 82120) mixes pyrites-cinders with 7 per cent. silicate of soda, moulds the mixture by pressing, and exposes it at a moderate temperature to the action of carbonic acid, by which free silica and sodium carbonate are formed. The silica acts as a cement; the sodium carbonate promotes the fusion of the slag, and prevents the sulphur contained in the cinders from passing into the pig-iron. [If the application of silicate of soda is not too expensive, its decomposition would be more easily and quickly obtained by the waste acid liquors formed at most works.]

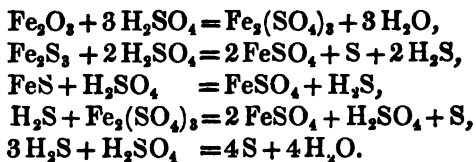
The Duisburg Copper-works (Germ. pat. appl. D 6242) mix pyrites-cinders with ground furnace scale (magnetic oxide of iron) or similar slags, if necessary also with lime, mould the mixture into bricks and dry these. According to whether lime has been employed or not, from 5 to 20 per cent. of slags is required. The product is sufficiently firm for use in blast-furnaces; owing to the admixture of slag, it is also porous and accessible for the reducing gases.

In England, bricks of purple-ore are made without any cementing substance, merely by strong pressure, for use in Siemens-Martin furnaces (Zsch. f. angew. Chem. 1894, p. 9).

A. & P. Buisine (Vol. II. p. 390) employ moistened pyrites-cinders for absorbing hydrogen chloride from gases containing very little HCl. Or else they convert them by heating with sulphuric acid into ferric sulphate (Compt. Rend. 1892, cxv. p. 51).

Buisine (Germ. pat. 73222) also describes a process for re-

covering from pyrites cinders ferrous sulphate and free sulphur by the following reactions:—



The ultimate products of these reactions, apart from steam, are only ferrous sulphate and free sulphur, which are easily separated.

Vol. I. p. 784. *Copper extraction from pyrites-cinders*.—Jurisch (Chem. Ind. 1894, p. 378) publishes very extensive notes, by the late E. A. Mebus, which do not modify our own description in any essential point, but which are of interest for those working in this special field. This especially holds good of the part referring to the recovery of silver.

Vol. I. p. 813. *Treatment of the copper liquor*.—Höpfner (Germ. pat. 66096) adds so much NaCl or CuSO<sub>4</sub>, that the proportion Na<sub>2</sub>SO<sub>4</sub> + CuCl<sub>2</sub> is attained; then he adds metallic copper, whereby all the copper is precipitated as cuprous chloride, together with the silver in the metallic shape. From the mother liquor, sulphate of soda is recoverable. Other modifications are also proposed.

Vol. I. p. 829. *Utilization of waste sulphate liquor from the wet copper extraction*.—Grabowski (Germ. pat. 71917) concentrates the liquor by evaporation and crystallization of Glauber's salt to spec. grav. 1.56; he then applies to them an electric current of great intensity, with lead and copper electrodes, by which arsenic and antimony are precipitated as metals at the cathode.

Brewer (Engl. pat. No. 1348, 1895) adds to the liquor a sufficient quantity of calcium-chloride solution, separates the resulting solution from the precipitated calcium sulphate (pearl-hardening), removes the silver, and afterwards the iron by calcium carbonate (in the shape of "caustic mud"), then nickel, cobalt, and manganese by bleaching-powder. This treatment practically leaves only the chlorides of zinc and calcium in the solution, which is electrolyzed in order to obtain metallic zinc and free chlorine.

Vol. I. p. 832. *Production of copper and precious metals from pyrites-cinders*.—Mr. John Hargreaves informs me of the following results, obtained in 1877 by the patent process, mentioned in the

text only by title. He treats the pyrites-cinders, obtained in the usual manner, in a closed chamber with fire-gases and excess of air, in order to burn all the residual sulphur; the mass is allowed to cool down to the point where no cupric chloride can be volatilized, and is then treated with gaseous HCl till it is sufficiently decomposed. It is then lixiviated with water in tanks, after being moistened with strong hydrochloric acid; the residual ferric oxide is obtained in lumps, which are immediately ready for the blast-furnace.

The cinders originally employed contained, according to the size of the grain, from 1.00 to 1.09 per cent. Cu in a shape soluble in water, 0.71 to 1.09 soluble in hydrochloric acid, 1.61 to 2.79 insoluble. They were passed through a sieve with 7 meshes per linear inch, and chlorinated as above described. The average from the upper part of the chamber then tested 3.90 per cent. Cu soluble in water, 0.63 soluble in weak hydrochloric acid, 0.56 insoluble; from the lower part of the chamber 3.51, 0.77, and 0.28 per cent. respectively. The treatment for burning the residual sulphur lasted from 26 to 96 hours, the chlorination from 24 to 72 hours. The liquors contained pretty much silver and a little gold; the washed residue contains only 0.8 to 0.12 per cent. copper. (I am not aware whether this process is now actually at work or not.)

Vol. I. p. 862. *Manufacture of fuming oil of vitriol (anhydrous sulphuric acid).*—At a large German works pure  $\text{SO}_2$ , obtained by the Schröder and Hänisch process, or in some other way, is mixed with the necessary quantity of air; the mixture is heated to the required temperature in a pipe-stove, and is then passed through an apparatus containing clay-balls impregnated with platinum black, similar to a Deacon decomposer (comp. this volume, p. 390). This apparatus requires no external heating, since the gaseous mixture develops heat in the combination of  $\text{SO}_2 + \text{O}$ , and needs only to be protected from cooling.

It is asserted that, by employing strong pressure by means of bronze blowing-engines (air-compressors), it is possible to make  $\text{SO}_2$  directly from pyrites-burner gas cheaply enough to employ it for bringing chamber-acid up to the strength of "rectified oil of vitriol," in lieu of concentration by evaporation, or even to manufacture ordinary sulphuric acid in this way, and thus to do away with lead chambers!

Vol. I. p. 865. *Fuming Sulphuric Acid produced by Electricity.*—Some more details respecting Léon's process, mentioned in the text, are given in his German patent No. 57118). He works in a cast-iron tank, cooled from without and covered with a slate slab. In the centre is the hollow platinum anode, with a water-cooled brass box inside. It is surrounded by an open, annular cathode, provided with open passages at the bottom, and supported by glass-coated copper rods, ending in platinum caps. With currents of very low density (0.1 amp. to 1 square centimetre), in which case the voltage can be lowered to 2.5, the electrodes are 3 centimetres high, and consist of crude copper, coated on both sides with platinum-foil soldered with gold; these are coiled in a spiral shape and kept at a proper distance by glass rods and asbestos cord. Per hour 1 kg. anhydrous acid [monohydrate?] can be produced with an expenditure of 0.9 H.P., or 1 kg. fuming acid of 68° Bé. with an expenditure of 1.2 H.P.

Vol. I. p. 865. *Analysis of fuming Sulphuric Acid.*—In Zsch. f. angew. Chem. 1895, p. 221, I have drawn attention to the fact that in allowing for the  $\text{SO}_2$  sometimes a serious mistake is committed. The  $\text{SO}_2$  is always tested for by iodine solution, and is then subtracted from the total acidity. Here we must consider that the neutrality-point in the case of phenolphthalein is reached when 1  $\text{SO}_3$  has been combined with 2  $\text{NaOH}$ , but in the case of methyl-orange only 1  $\text{NaOH}$  is consumed for 1  $\text{SO}_3$ . Litmus cannot be used at all, as it gives uncertain results between these two limits. With methyl-orange 1 c. c. normal soda solution indicates 0.040 gram  $\text{SO}_3$ , but 0.064 gram  $\text{SO}_3$ . Hence for each c. c. of decinormal iodine solution only 0.05 c. c. of normal, or 0.1 c. c. of semi-normal solution of  $\text{NaOH}$  must be deducted. If this is overlooked, a very serious mistake is committed; for since everything which is not present as  $\text{SO}_3$  or  $\text{SO}_2$  is assumed to be water, the incorrect allowance for  $\text{SO}_2$  will cause not merely a deficiency of  $\text{SO}_3$ , but a surplus of  $\text{H}_2\text{O}$ , and as this must be represented as combined with 4.444 its weight of water, far too little free  $\text{SO}_3$  is found.

A practical instance will illustrate this. 3.5662 grams fuming acid were diluted to 500 c. c. and 100 c. c., = 0.71124 gram, employed for each test. This consumed 5.40 c. c. iodine solution, =  $5.40 \times 0.0032 = 0.01728$  gram  $\text{SO}_2$  or 2.43 per cent.  $\text{SO}_2$ . On titrating with semi-normal soda solution and methyl-orange,



34.40 c. c. was used. By erroneously deducting  $0.2 \times 5.40 = 1.08$  c. c., there remained 33.32 c. c.  $= 0.6664$  gram  $\text{SO}_3$  or 93.70 per cent. The fuming acid therefore would have contained 93.70 per cent.  $\text{SO}_3$ , 2.43  $\text{SO}_3$ , 3.87  $\text{H}_2\text{O}$ . The 3.87  $\text{H}_2\text{O}$  is  $= 17.20 \text{ SO}_3$ , and the free  $\text{SO}_3$  would be  $= 93.70 - 17.20 = 76.50$  per cent.

In reality the 5.40 c. c. decinormal iodine corresponds to only 0.54 c. c. seminormal soda, leaving 33.86 c. c.  $= 0.6772$  gram  $\text{SO}_3 = 95.21$  per cent. Composition of the acid: 95.21 per cent.  $\text{SO}_3$ , 2.43  $\text{SO}_3$ , 2.36  $\text{H}_2\text{O}$ . The 2.36  $\text{H}_2\text{O}$  is  $= 10.49 \text{ SO}_3$ , leaving  $95.21 - 10.49 = 84.72$  per cent. free  $\text{SO}_3$ . Hence by that erroneous calculation the factory committed an error of 8.25 per cent. to its own disadvantage!

Exactly the same result is obtained when performing the calculation by the aid of Guehm's table (Vol. I. p. 870); but the use of this table involves far more trouble and time than the direct calculation as above, where  $\text{SO}_3$  has to be allowed for (which is always the case in practice).

We have, as already mentioned, assumed everything as  $\text{H}_2\text{O}$  which has not been found to be present as  $\text{SO}_3$  and  $\text{SO}_2$ . But it is advisable to estimate the *fixed impurities* as well, since otherwise their weight, multiplied by 4.444, is erroneously deducted from the free  $\text{SO}_3$ .

Vol. I. p. 875. *Preparation of Sulphuric Acid by Electrolysis of Sulphurous Acid*.—Wacher (Germ. pat. applic. W 10532, 1894, and 10591, 1895) proposes to prepare concentrated sulphuric acid by electrolyzing water or dilute sulphuric acid, through which a continuous stream of  $\text{SO}_2$  is being passed. He employs an earthenware vessel, divided into two cells by a porous earthenware diaphragm. Into the anode cell a slow stream of  $\text{SO}_2$  is introduced. In the cathode cell a magma of sulphur is formed, but little  $\text{H}_2\text{S}$  being given off. If hydrochloric acid is added, no sulphur is separated, the chlorine formed by electrolysis directly oxidizing the  $\text{SO}_2$ . Other oxygen carriers may also be employed, such as sodium chloride or sodium sulphate, which acts by forming persulphuric acid; or else chlorates, nitrates, and so forth. [This process, in its present form, is a very peculiar one.]

Vol. I. p. 875. *Barbier's apparatus for manufacturing Sulphuric Acid* consists of six towers, arranged in steps, packed with hollow pieces of sandstone, quartz, or the like. Burner-gas enters the bottom tower and passes through them all. The towers are

connected alternately at top and bottom; the last serves as Gay-Lussac. Nitrous vapours and steam are introduced from a concentrating-pan fired from without. The acid formed in the towers drops into concentrating-pans placed below their open bottoms, or into a collecting-vessel. They are fed with a mixture of sulphuric and nitric acid, if necessary also with steam. Private reports concerning Barbier's apparatus mention an excessive consumption of nitric acid and also obstructions. The high royalty has also acted as a check upon experiments with it. Candiani (Chem. Ind. 1895, p. 153) remarks that the only Italian factory which had introduced Barbier's process had not been very successful with it. Boissieu (Bull. Soc. Chim. (3) xi. p. 726) asserts that the Barbier system has answered very well, but he unfortunately does not quote any figures or other proofs for this assertion.

Staub (Engl. pat. 12675, 1894) describes a set of five towers, packed with specially moulded earthenware pieces, and fed with nitric acid, nitrous vitriol, &c.

In several places experiments are planned or in progress for making sulphuric acid entirely without chambers. This is mostly done with imitations of the "plate-columns" ("Lunge towers"). Theoretically all such apparatus will enable sulphuric acid to be made. But up to the present I consider it preferable to build a lead chamber, say one third of the ordinary size, behind the Glover tower, in which the intense reaction takes place and the steam from the Glover tower is utilized. Then follow one or more plate-columns, fed with dilute acid ( $30^{\circ}$  to  $40^{\circ}$  B $\acute{e}$ . =  $52^{\circ}$  to  $76^{\circ}$  Tw.), which furnishes the water for the formation of sulphuric acid, gases, vapours, and mist being brought into intimate contact with it. If necessary, of course, water, nitric acid, or nitrous vitriol may be introduced here as well. Between the plate-columns and the Gay-Lussac towers a small lead chamber would be useful for drying and cooling the gas.

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VOL. II. pp. 30 and 65. *Natural occurrence of Sulphate of Soda in Wyoming, U.S.*—Detailed communications respecting this are made by Attfield, Journ. Soc. Chem. Ind. 1895, p. 3.

Vol. II. p. 61. *Natural Soda*, containing no sulphate and hardly any chloride and iron, is stated to occur in German East Africa (Journ. Soc. Chem. Ind. 1895, p. 616).

Vol. II. p. 107. *Commercial alkalimetical degrees.*—As mentioned in the text, I many years ago opposed the utterly fallacious "Liverpool test," and I was severely criticized for doing so. Unfortunately the hope which I then expressed, that this test was no longer in use, seems to have been unfounded; for according to the 31st Alkali Report, p. 67, Castner furnishes electrolytically made caustic soda at 78 to 79 per cent., Liverpool test, whereas chemically pure NaOH would only test 77·50 per cent. real Na<sub>2</sub>O!

Vol. II. p. 206. *Nuisance in drawing the saltcake out of the furnace.*—The pungent vapours inevitably given off during this operation, which at all events greatly distress the workmen, even when they are prevented from being a nuisance to the neighbourhood, are entirely prevented by allowing a fine spray of water to play upon the hot saltcake, at a distance of about three feet, from a jet exactly like those very advantageously used in the vitriol-chambers, and described Vol. I. p. 424, fig. 166. This fine spray condenses the vapours to such an extent that (as I have convinced myself) no smell is perceptible close by, and does not cause the hot sulphate to become damp. There is steam, but no "gas." This simple contrivance deserves serious attention with a view to preventing nuisance.

Vol. II. p. 208. *Special ways of manufacturing saltcake.*—Walker (Engl. pat. No. 22853, 1854) mixes with common salt sufficient sulphuric acid to form an acid sulphate, which is treated in one of the following ways:—Either it is cooled, roughly ground, mixed with monosulphate and salt, and heated in a second furnace with a mechanical stirrer; or else it is run out of the first furnace in the fused state over a weir into another compartment, where the above mixture also takes place. To obtain nitric acid, nitrate of soda is treated in the same manner. [Neither of these processes has any economical value.]

Vol. II. p. 225. *Continuous mechanical saltcake pot and furnace.*—Thomson and Worsley (Engl. pat. Nos. 21945 and 21946, 1894) employ two decomposing-pots to each roasting-furnace. These pots are fitted with stirrers and automatic charging-apparatus, by which the supplies of salt and vitriol are regulated so as to keep the vitriol in excess. The charge, which remains sufficiently liquid, flows through a pipe above the level of the agitator into the roasting-furnace. This is a round muffle-furnace,

heated above and below, the revolving top carrying stirrers and ploughs, which mix and gradually move the charge towards the outlet, where it is continuously and automatically discharged. As the charge passes from the pot into the furnace, more salt is added by a conveyer-worm, in proportion to the excess of acid in the pot. Thus a continuous stream of hydrochloric acid is evolved, nearly free from water-vapour, and fit for the manufacture of chlorine by the Deacon process without further drying.

Vol. II. p. 236. *Percentage of iron in commercial saltcake.*—Ost (Zsch. f. angew. Chem. 1896, p. 9) found, in eight samples of saltcake made by the ordinary process in iron decomposing-pots, from 0·066 to 0·130 per cent. iron; in three samples made in lead pans, from 0·009 to 0·029 per cent. iron. All of these are from German works (of which 24 decompose salt for the manufacture of saltcake). The plate-glass works require a guarantee that the iron does not exceed 0·05 per cent.

Vol. II. p. 278. *A modification of the Hargreaves process* by Bassett and Baranoff (Engl. pat. 21447, 1894) produces the  $\text{SO}_2$  intended for decomposing the  $\text{NaCl}$  as follows:—Calcium sulphate (natural or artificial) is mixed with carbon and heated in a retort; the  $\text{CO}_2$  given off is utilized later on. The calcium sulphide formed is moistened with water, and is then subjected, in an apparatus similar to that used for making bleaching-powder, to the  $\text{CO}_2$  from the first reaction. The  $\text{H}_2\text{S}$  evolved is burned into  $\text{SO}_2$  and utilized for decomposing  $\text{NaCl}$ . The residual calcium carbonate is roasted for the liberation of the  $\text{CO}_2$  it contains.

Vol. II. p. 367. *Packing of Hydrochloric Acid condensers.*—Doulton and Sanceau (Engl. pat. 14766 and 14768, 1894) patent the old system of pottery towers packed with perforated short cylinders, and perforated discs laid upon these, or tiles perforated in various ways, for the condensation of hydrochloric and nitric acid. Precisely the same thing is mentioned in the first edition of this work, and again in the second edition, *loc. cit.*

Barbier (Engl. pat. 14014, 1894) describes a special packing for condensing-towers, consisting of inverted cells with perforated ends, of cylindrical or truncated cone shape; a vertical central cooling-shaft supplies cold air. The perforated ends of the cells are made concave to retain any solid particles carried over.

Vol. II. p. 369. *Feeding-apparatus for acid-condensers.*—Schüler (Zsch. f. angew. Chem. 1895, p. 373) modifies the appa-

ratus of Raulin, described in the text, in a very judicious way. He divides the inner limb of the siphons into two branches, one of which dips into an open cup: by means of this arrangement the siphon empties itself completely at every run, and no frothy mixture of air and water is formed. The inside diameter of the siphons is best  $=\frac{1}{2}$  inch. The dimensions of the various vessels are planned so that for a certain setting of the tap they are all filled at the same time, *e. g.*, in 80 seconds; this can be altered at will by a different setting of the tap, and the quantity of water is easily measured in the same way. Schüler prefers as dividing-apparatus the acid-wheel with a glass bulb floating on concentrated sulphuric acid (p. 783), and a bell announcing every revolution (Vol. I. p. 526), to the fixed overflow apparatus and splash-plates.

Vol. II. pp. 382 and 916. *Plate-towers for condensing Hydrochloric Acid*.—Lasche (Zsch. f. angew. Chem. 1895, p. 374) reports further trials with the Lunge-Rohrmann plate-towers, a little wider than those originally employed by him (comp. Vol. II. p. 916), viz. 0·803 metre, but otherwise constructed in the same way, viz., with annular bearers and quartz packing between these and the outside pipes. Each tower possessed 30 plates with 7 mm. holes, and 30 with 60 mm. holes. The acid obtained averaged 20°·1 Bé. ( $=32^{\circ}\cdot 5$  Tw.) at 15° C. The yield was 169·3 parts to 100 rock-salt. By removing 8 plates and putting on 6 feet of coke, the yield was increased to 183 or 184 parts of acid. Lasche ascribes the necessity of employing this layer of coke to the strong draught required; but he believes that it would be unnecessary in the case of plus-pressure furnaces (Vol. II. p. 191) or when employing the new description of cylinders shown fig. 304, Vol. II. p. 920, by which the annular bearers and the quartz packing are abolished. [Considering the slight cost of this small layer of coke and its usefulness, as explained Vol. II. p. 916, I would recommend retaining it.]

Niedenführ (Chem. Zeit. 1896, p. 33) confirms from his own experience the excellent results obtained elsewhere by Lasche with the Lunge-Rohrmann plate-towers in the condensation of hydrochloric acid, which in his case was rendered more than usually difficult by the employment of waste acid from the refining of petroleum for decomposing the salt, entailing a copious evolution of sulphur dioxide.

Vol. II. p. 408. *Pulsometers for pumping acids*.—P. Kestner, of Lille, has greatly improved the pulsometers described in the text, especially by modifying the valves, which are no longer in contact with the acid and are made of gun-metal. These new pulsometers are used both for sulphuric acid and, made of ebonite, for hydrochloric acid.

Vol. II. p. 426. *Carriage of Hydrochloric Acid*.—Kramer (Engl. pat. No. 4684, 1895) proposes wooden receptacles, lined first with a mixture of asbestos and silicate of soda, and afterwards with paraffin-wax, pitch, coal-tar, &c.

Vol. II. p. 429. *Manufacture of Hydrochloric Acid*.—Lorenz (Engl. pat. 25073, 1894) proposes making hydrochloric acid from electrolytically or otherwise obtained free chlorine, by passing the chlorine simultaneously with steam through earthenware retorts, charged with coke, charcoal, anthracite, or the like, and heated to a dark red heat. The reaction  $2\text{Cl} + \text{H}_2\text{O} + \text{C} = 2\text{HCl} + \text{CO}$  is stated to take place easily and quantitatively; the CO can be employed for heating the retorts. [At present, of course, such a process is utterly impracticable in an economical sense; but it is impossible to say whether the future may not bring about such changes of values as to make it remunerative to turn Cl into HCl; comp. p. 710.]

Vol. II. p. 593. *Lixiviation of black-ash*.—The process described here as best for the lixiviation of revolver-ash, viz. beginning with cold water and raising the temperature of the strong tank by injecting a little steam (preferably into the overflow from the preceding tank), is employed at many works for hand-made ash as well, and with the best results. It is quite possible to operate in such a way that the sulphide and sulphate in the liquor do not exceed that found by testing the black-ash in the laboratory, and thus, with very good sulphate and faultless balls, to turn out all the soda-ash at 57 per cent. real (not "Liverpool") strength, as the best German and some English works do. But for this purpose it is necessary not to exceed  $50^{\circ}\text{C}$ . even in the strong tank; and at this comparatively low temperature it is only when the balls are as porous as possible that they can be completely washed. The secret of this seems to lie in forming as much caustic lime as possible in the ball-furnace, which can be effected only by working it at the greatest heat attainable. The caustic lime, by slaking as the black-ash is brought into contact with water, swells up and

causes the dense mass to be thoroughly loosened. It would appear that this cannot be done to a sufficient extent by a *mechanical* mixture of lime, *i. e.* Mactear's process (Vol. II. p. 543), but only by applying enough heat to causticize a sufficient quantity of the excess of calcium carbonate intimately mixed with the sodium carbonate in finished black-ash. Although black-ash made in this way contains more caustic lime than that made at a lower heat, yet the liquor obtained from it contains less caustic soda, because, on account of the much looser state of the black-ash, the lixiviation takes place more quickly and at a lower temperature. The caustic soda in itself is not a very serious evil, as it can be completely removed by proper carbonating; but along with an excess of it, owing to the higher temperature and longer duration of lixiviation, a good deal of sodium sulphide is also formed, thus seriously deteriorating the quality of the soda-ash.

Vol. II. p. 609. *Carbonating the soda-liquors and finishing the ash.*—This process is carried on at Griesheim as follows:—The liquor is first thoroughly settled on the continuous plan, by running it through a number of large tanks, each continually overflowing at the opposite end into the next. The perfectly clear liquor is run down an iron column filled with coke. Into this enters the gas from a boiling-down pan for soda-crystal mother-liquor, heated from the top. This gaseous mixture of  $\text{CO}_2$ , O, N, &c. is consequently always saturated with moisture; so that the liquor is *not* concentrated in the carbonating-tower. This is of importance, as it has been found that liquors above  $50^\circ$  Twadd. are not easily carbonated through. The gas is aspirated by a small air-pump, and forced into the tower at the top, escaping at the bottom into a flue leading into the chimney. If the gas enters at the bottom, crusts are formed very quickly, which partially stop up the interstices between the pieces of coke. If the plan just described be employed, the coke can go for several months before it need be taken out. This pumping of gas through a coke-tower takes very much less power than the Ludwigshafen process (p. 609), where the  $\text{CO}_2$  is forced through a column of liquor.

The result of the process is ascertained by testing the liquor with turmeric paper. This turns yellowish red so long as even a trace of caustic remains in the liquor, but much more deeply brownish red when there is no caustic present. To make sure, the colour

of the paper is always compared with that of another paper dipped into a strong solution of pure sodium carbonate; only when the two papers are quite alike in colour is the process stopped and the liquor (which now contains a little bicarbonate) run off.

Although the carbonating takes place with thoroughly settled tank-liquor, it is found that after carbonation the liquor, on being heated, deposits many impurities. The carbonated liquor therefore, before entering the Thelen fishing-pan (Vol. II. p. 653), is run through three or four tanks in succession, in which it is gradually heated up to  $80^{\circ}\text{C.}$ , as the waste heat of the pan-fire (which itself is only the waste fire of a black-ash furnace) passes underneath them; and on its way again a good deal of deposit is formed, which of course must not be disturbed until it is time to remove it from the tanks.

The salt formed in the mechanical fishing-pans (which in this instance cannot possibly be called "black-salt") is almost pure monohydrated sodium carbonate; it is constantly taken out by the scrapers, and carried over the side of the pan, along with a little mother liquor. Even the latter, owing to the careful work, is so pure that it is either made into caustic soda of high strength *without any salting out*, or into soda-crystals, the last mother liquor of which still yields soda-ash of 90 per cent.  $\text{Na}_2\text{CO}_3$ . The drained salt itself is best dried in any ordinary calcining furnace or in the new Thelen pan (Vol. II. p. 662, and Vol. III. p. 88) without any trouble, as it is quite free from caustic and sulphides; it yields regularly soda-ash of 98 per cent.  $\text{Na}_2\text{CO}_3$ . At Griesheim another mode of drying was preferred, with the object of both economizing fuel and obtaining perfectly white soda-ash without having to destroy the cyanogen compounds. The salt is dried, at a heat not exceeding  $150^{\circ}\text{C.}$ , in cast-iron retorts exactly similar in size and shape to gas-retorts. Each retort yields 4 cwt. of ash. They are set in rows and heated by a portion of the waste heat from the black-ash furnace, which has also done the boiling-down; so that both the boiling-down and finishing of the ash require no fuel whatever. Care must be taken that the heat does not exceed  $150^{\circ}\text{C.}$ , at which point the sodium ferricyanide is not yet decomposed, and therefore the ash is not discoloured at all. If any of the retorts are allowed to get too hot, the salt begins to colour at once; but this is easily avoided, as the fire-gases have been previously cooled down so much underneath the boiling-down pans.



This plan requires also much less manual labour than the ordinary practice of boiling-down and finishing.

Vol. II. pp. 653 and 662 (also Vol. III. p. 88). *Thelen pans*.—According to information received from the Rhenania Chemical Works in 1895, an evaporating-pan furnishes  $2\frac{1}{2}$  to  $3\frac{1}{2}$  tons soda-ash per 24 hours, with a consumption of 10 cwt. of coal and 1s. for wages per ton. One man can attend to three pans, if coal and ashes are carted for him; or upon five pans, if the heating is performed by waste heat from a black-ash furnace. The pan weighs  $4\frac{1}{2}$  tons, the machinery  $7\frac{1}{2}$  tons; power required  $\frac{1}{4}$  H.P.

A drying-pan and mill furnish in 24 hours 10 tons soda-ash, with a consumption of  $\frac{3}{4}$  to 1 cwt. of coal, and 8d. for wages per ton. One man does all the work connected with the apparatus, inclusive of packing the soda-ash. Weight of shafting, &c.,  $3\frac{1}{2}$  tons, of machinery  $7\frac{1}{2}$  tons, of the cast-iron pan 9 tons (in the case of ammonia-soda pans the weight of the cover must be added to this). Power required,  $\frac{1}{2}$  H.P.

Vol. II. p. 711. *Improving the colour of soda-crystals*.—Three persons named Peak and a Mr. Haddock, by their united efforts, have secured an English patent (No. 14894, 1894) for improving the colour of soda-crystals by adding to the liquors, just before they begin to crystallize, about one part of methylene blue B to every 4000 parts of the soda liquor! The novelty of this "invention" is about equal to its value.

Vol. II. p. 714. *Manufacture of bicarbonate of soda*.—The following process by Carthaus (Germ. pat. 79221) is evidently intended for pharmaceutical purposes, as it would be otherwise too dear. Magnesite or dolomite is burned and treated with water and carbonic acid under pressure, in which case only magnesium bicarbonate is dissolved. Sodium chloride or strong brine (which need not be free from  $MgCl_2$ ) is gradually added to this solution, sometimes together with ammonium salts. Sodium bicarbonate is precipitated and is separated from the mother liquor, containing magnesium chloride, by a centrifugal machine or by a filter-press working with compressed carbonic-acid gas. It is best to perform the work in cylindrical vessels made of earthenware, or of iron with an inside lead coating and agitating-gear.

Vol. II. p. 744. *Causticizing soda-liquors*.—Neuendorf (Germ. pat. 81923) treats the solution of sodium carbonate with a mixture of calcium carbonate and caustic lime, separates the liquor from

the mud, and finishes the operation by treating with fresh lime. Thus in the first process all the lime is converted into carbonate, and in the second a mixture is obtained which is employed in the first stage of the next operation. [This very old process, viz., using up the partially-spent lime in the initial stage of the next operation, has been described already in the first edition of this book as a matter of course. It is evidently identical with the English patent No. 3485, of 1895, taken out by Imray for the Chemische Fabrik Rhenania.]

Vol. II. p. 755 (comp. also p. 879). *Employment of lime-mud from causticizing soda for the manufacture of Portland cement.*—Rigby, Neill, and Carr (Germ. pat. 82499) mix this mud intimately with clay, and heat the mixture until it has become dark-coloured and dense. [Where is the novelty?]

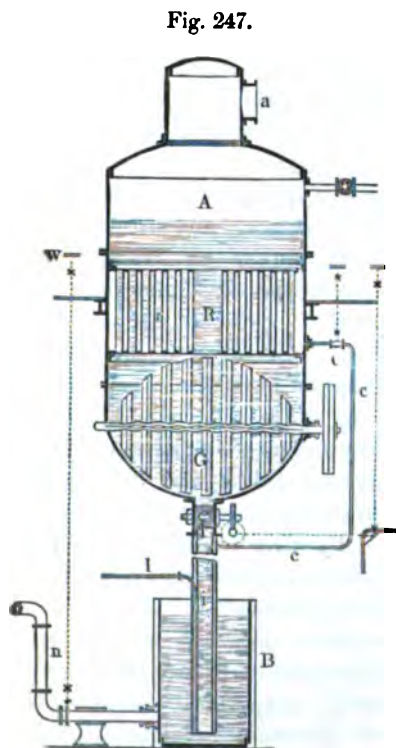
Vol. II. p. 765. *Multiple-effect evaporating-pans.*—For evaporating caustic-soda liquors, both in the case mentioned in the text and in electrolytic processes, vacuum apparatus in *which the salts can be removed without interruption of work* are especially suitable. Several apparatus of this kind have been constructed, of which we describe the following.

Fig. 247 shows the apparatus of the Kaliwerke Aschersleben (Germ. pat. 34034). Boiler A is connected by branch *a* with the air-pump; the liquor runs in through *l*. Tap *d* can be closed by the dotted gearing, in order to prevent A from running empty in case the work stops. The downward pipe *i*, provided with a heating-jacket, must be long enough for the outer atmospheric pressure to balance the liquor contained in this pipe and in A; if two or three boilers work in series, this pipe must have a different height in each of them.

The water formed in the heating-jacket round *i* runs off by *l*. The depth of liquor in B is regulated by the pipe *n*, which can be turned from *w*. While tap *d* is open, A is filled by running the liquor in from below, the air being exhausted through *a*. Then steam is put on, and the liquor in A is brought to the proper height. The contents of A are kept stirred by G, and hot water or steam is passed through *c* into the heating-jacket round *i*, the tap on pipe *l* being opened to the extent required for an uninterrupted feed of fresh liquor. The heating-pipes *r* and the central pipe R produce a continuous circulation of the liquor in A, so that the specifically heavier liquor and the salts

separating therefrom arrive at the bottom, where they are kept stirred by G and ultimately sink through *i* into B, from whence the concentrated liquor with the crystals runs off through *n*. The latter is made movable in order to set it, according to the changing pressure in A, in such manner that the liquor runs off at the proper time.

Fig. 248.



**Kaufmann's vacuum-pan** (Germ. pat. 75421) renders it possible to remove the salts, without interfering with the vacuum, by means of a mechanical agitator. In the specially-shaped lower part

of the apparatus, fig. 248, is placed an agitating arrangement R, exactly fitting upon it. This agitator is driven from without by means of a shaft, turning in a stuffing-box, with a circumferential velocity  $v$ , calculated by the following formula :— $v^2 > \frac{p}{\gamma} 2g$ , where  $p$  is the height of vacuum expressed in metres of water,  $\gamma$  the specific gravity of the salt,  $g$  the acceleration by the force of gravity. Thus the salt is removed under the pressure of the atmospheric air. For instance, assuming the diameter of the agitator = 1·8 metres, the vacuum within the apparatus = 0·6 metre (= 8 metres water), the specific gravity of the salt = 1·4, the number of revolutions should be 108 per minute. The rotation of the agitators in the preliminary evaporators must be adapted to the tensions of each of them. The salt is removed by the exit-branch either periodically or continuously.

Vol. II. p. 768. *Treatment of caustic salts*, obtained in evaporating caustic liquors.—Brock, Driffield, Carey, and Brown (Engl. pat. 3037, 1894) remove the caustic liquor by draining and steaming as much as possible, and introduce the moderately dry salt through an opening in the side of a revolving horizontal cylinder. Hot lime-kiln gas is passed in through one of the hollow journals, and is conveyed away through the other journal into a condensing-chamber, cooled by water, from the bottom of which the gas escapes into another cylinder, where it is used over again. If pure carbonic acid is at disposal, it can be made to circulate quickly between the revolving cylinder and the condenser by means of a fan-blast. By this treatment the salts absorb carbonic acid, and can then be converted into commercial soda-ash by calcining in a reverberatory furnace.

Vol. II. p. 792. *Accidents to workmen caused by caustic soda*.—Any burns caused by caustic soda on the skin are best treated by the well-known domestic remedy, prepared by shaking up equal volumes of lime-water and linseed-oil. The Chemical Works Commission of Inquiry of 1893 recommends, in the case of burns on the mucous membrane of the eye &c., to wash out the caustic soda with pure water by means of a squirt or wash-bottle. Jurisch recommends instead of this a solution of acetate of lead as far superior, and actually in use at some chemical works. The Commission demands that every uncovered pot containing liquid of a dangerous character shall be at least 3 feet in height above

the ground, or, where that is impossible, it must be fenced in. There must be a clear space all round; there is to be no footing on the top or sides of the brickwork, and dome-shaped lids are to be used where possible.

Vol. II. p. 798. *Packing the caustic into drums*.—At Griesheim this is done in a very expeditious and cleanly manner by means of a tramway running parallel with the caustic-pots, at a short distance from them. The tramway is sunk so that the small bogies running upon it are level with the ground. The drums, standing upon the bogies, are run underneath the shoot one after another, the shoot being a little raised at the lower end when the drum is full, and lowered again when the next drum has taken its place. Otherwise the shoot always remains in the same place from beginning to end.

Vol. II. p. 806. *Vanadium in caustic soda*.—Robinson (Chem. News, 1894, n. lxx. p. 199) found in a sample of caustic soda 0·0211 per cent. Va.

Vol. II. p. 804. *Packing caustic soda*.—Jänecke and Schneemann (Germ. pat. 77237) protect caustic alkalies against the access of air by a layer of melted saltpetre or other easily fusible salts.

Vol. II. p. 824. *Utilization of tank-waste*.—Loesner (Engl. pat. No. 16407, 1895) employs the calcium sulphide contained in tank-waste as an agent for reducing nitrobenzene &c. to aniline, by heating four parts of nitrobenzene for from four to eight hours with six parts of calcium sulphide and five to ten of water. This method is stated to produce a larger yield of aniline than the ordinary method of reduction by iron and hydrochloric acid; the yellow colour of the aniline obtained can be removed by distilling the latter.

Vol. II. p. 878. *Protection against poisoning by sulphuretted hydrogen*.—The English Commission of Inquiry (1893) recommends respirators, charged with moist oxide of iron, to be kept in readiness for those men who have to rescue people from a place filled with sulphuretted hydrogen, and compressed oxygen to be kept in stock for the artificial respiration of people rendered unconscious by inhaling sulphuretted hydrogen.

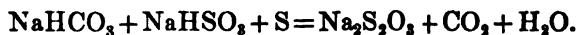
Vol. II. p. 891. *Sulphur from hydrogen sulphide and sulphur dioxide*.—Bémelmans (Germ. pat. 77335) mixes and heats both gases in the dry state, and only then causes the well-known de-

composition into S and  $\text{H}_2\text{O}$  by introducing steam. The  $\text{H}_2\text{S}$  is to be cooled and passed in a current, not exceeding a velocity of 0·5 metre per second, through towers filled with porous calcium chloride. The  $\text{SO}_2$  is also cooled and dried in a coke-tower by means of sulphuric acid. Both gases are now mixed and heated to  $100^\circ \text{C}$ . in a zigzag flue, by means of water-gas; on issuing, they are carried by a steam-jet into a condenser, where under these circumstances the reaction  $\text{SO}_2 + 2\text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}$  is said to occur completely.

Farbaky (Fischer's Jahresb. 1894, p. 431) gives a detailed description of the manufacture of sulphur from  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in Schaffner towers fed with a solution of calcium chloride. The  $\text{H}_2\text{S}$  is derived from dissolving lead matte in sulphuric acid, the  $\text{SO}_2$  from burning pyrites smalls.

Vol. II. p. 896. *Recovery of Sulphur by the Claus process.*—The Alkali Report, No. 31, p. 13, proposes to construct the chamber for condensing the subliming sulphur not of brickwork, which is soon acted upon by the acids, but of lead with a wooden framework, like a vitriol-chamber.

Vol. II. p. 908. *Manufacture of Thiosulphate in the dry way.*—Sidler (Germ. pat. 81347) heats a mixture of sodium bisulphate, sodium bicarbonate, and sulphur to  $120^\circ$  or  $130^\circ \text{C}$ .  $\text{CO}_2$  is given off and thiosulphate formed:



Vol. III. p. 178. *Caustic soda from common salt by barium sulphate and ferric oxide.*—Knobloch (Germ. pat. appl. K 12263, 1894) heats 1 part ferric oxide with 4 parts barium sulphate to the fusing point and adds 2 parts common salt, heating until most of the iron has volatilized as ferric chloride. The residue consists mostly of barium oxide and sodium sulphate. On treating it with water, caustic soda is formed and barium sulphate is re-formed. The ferric chloride is decomposed by steam and heat into  $\text{HCl}$  and  $\text{Fe}_2\text{O}_3$ , or by air and heat into free chlorine and  $\text{Fe}_2\text{O}_3$ .

Vol. III. p. 548. *Chlorate of soda.*—Hargreaves and Bird (Engl. pat. 18526, 1894) manufacture this by passing chlorine through a solution of sodium hydrate, carbonate, or bicarbonate. Their process is quite similar to that of Best and Brock, mentioned in the text, patented shortly after theirs.

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